Strategies for the removal of lignin derived impurities from *Eucalyptus globulus* wood prehydrolyzates

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„Alles Wissen und alles Vermehren unseres Wissens endet nicht mit einem Schlusspunkt, sondern mit einem Fragezeichen.“

Hermann Hesse (1877-1962)

Acknowledgment

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Abstract

The autohydrolysis of wood, as a first step of dissolving pulp production leads to the extraction of hemicelluloses that need to be removed for dissolving pulp applications and thus yields a hydrolyzate rich in oligomeric sugars that can be converted to valuable products. During the autohydrolysis step also lignin dissolves which partly precipitates upon cooling and tends to form sticky incrustations which hinder the hemicellulose recovery.

It was the scope of this thesis to reduce lignin dissolution itself, or to find possibilities to remove the lignin from the hydrolysis liquor directly after autohydrolysis to prevent scaling. Acid catalysis of the autohydrolysis reaction with sulfuric and oxalic acid and the resulting low temperatures reduced the amount of lignin precipitates, but did not alter the soluble lignin content. Furthermore the hydrolysis of oligomeric carbohydrates to monomeric sugars was significantly enhanced, which leads to a distinctly different product spectrum. Because of the low efficiency of lignin reduction during acid catalysis, a series of adsorbents was evaluated. At room temperature activated charcoal showed high efficiency and selectivity towards the removal of lignin derived products. These good results were even exceeded at a prehydrolysis temperature of 170 °C, which goes against the common physical understanding of the thermodynamics of adsorption. The highly efficient adsorption of lignin at high temperatures was attributed to polymerization reactions enhanced by the charcoal surface and to the chemisorptive binding of the lignin, which was justified by the low solubility of adsorbed lignin in solvents that normally show a high capacity for lignin dissolution.

For the application of high temperature adsorption of lignin on charcoal (HiTAC-process) in industry, it was necessary to find appropriate recycling strategies for the charcoal. Thermal reactivation of spent charcoals at 950 °C in CO_2 atmosphere yielded a charcoal that had properties similar to the fresh charcoal in respect of the pore size distribution and the selective adsorption behaviour. Generally, it was shown that charcoals with high volumes of small micropores and low volumes of mesopores showed the best efficiency towards lignin adsorption, and maintained high concentrations of carbohydrates in the hydrolyzates.

Zusammenfassung

Die Autohydrolyse von Holz als erster Schritt eines Holzaufschlussverfahrens ermöglicht die Extraktion von Hemizellulosen, deren Entfernung zum Einen notwendig ist um Chemiezellstoff herzustellen, zum Anderen können aus den gelösten Xylooligosacchariden wertvolle Produkte gewonnen werden. Beim Prozess der Autohydrolyse werden allerdings auch Ligninkomponenten aus dem Holz gelöst, die zu einer starken Verkrustungsbildung neigen. Ein Teil dieses Lignins fällt beim Abkühlen der Hydrolysate aus. Ziel der vorliegenden Dissertation war es, Möglichkeiten zu finden, die Lösung des Lignins auf ein Minimum zu beschränken beziehungsweise das Lignin möglichst direkt nach erfolgter Autohydrolyse aus den Hydrolysaten zu entfernen. Durch saure Katalyse der Autohydrolyse mittels Oxal- und Schwefelsäure gelang es den bei Raumtemperatur unlöslichen Teil des Lignins zu reduzieren, der lösliche Teil hingegen wurde durch die geringeren Temperaturen, die durch die Katalyse möglich sind, kaum beeinflusst. Durch die Zugabe von Säure wurden die Geschwindigkeiten der Hydrolysereaktionen stark erhöht, sodass die Oligosaccharide in Lösung sofort weiter zu monomeren Zuckern gespalten wurden. Da die Säurekatalyse der Vorhydrolyse in Summe nur zu einer unwesentlichen Ligninreduktion führte, wurden unterschiedliche Adsorptionsmittel zur Ligninentfernung evaluiert. Bei Raumtemperatur konnte eine hohe Effizienz und Selektivität der Ligninadsorption an Aktivkohle erreicht werden, die bei der Ligninadsorption bei 170 °C sogar noch übertroffen wurde. Die gute Effizienz der Ligninadsorption bei hohen Temperaturen, die so nicht erwartet wurde, da sie im Gegensatz zur Thermodynamik steht, kann mit der Polymerisation des Lignins auf der großen Oberfläche der Aktivkohlen begründet werden. Zusätzlich chemosorbiert Lignin auf der Aktivkohle, was zu einer schlechten Desorbtion des Lignins mittels Ligninlösungsmitteln führt. Um den Adsorptionsprozess zur Ligninentfernung auch industriell anwenden zu können, wurde nach Möglichkeiten gesucht, die Aktivkohlen nach der Adsorption wieder zu regenerieren. Thermische Reaktivierung bei Temperaturen von 950 °C unter CO_2-Atmosphäre führte zu einer Aktivkohle, die sowohl in ihrer Porenverteilung als auch in ihrem Adsorptionsverhalten frischer Aktivkohle gleich kam. Grundsätzlich konnte gezeigt werden, dass Aktivkohlen mit großen Volumina an kleinen Mikroporen und einer geringen Anzahl an Mesoporen Lignin am selektivsten adsorbieren, während die Kohlenhydrate in Lösung bleiben.

List of publications

This thesis is based on the following papers which are referred to in the text by the roman numerals:

I. Gütsch, J.S., Sixta, H. (2011) Purification of Eucalyptus globulus water prehydrolyzates using the HiTAC process (high-temperature adsorption on activated charcoal). Holzforschung 65:511-518

II. Gütsch, J.S., Sixta, H. (2011) The HiTAC-process (high temperature adsorption on activated charcoal) - new possibilities in autohydrolysate treatment. Lenzinger Berichte 89:142-151

III. Gütsch, J.S., Nousiainen, T., Sixta, H. (2012) Comparative evaluation of autohydrolysis and acid-catalyzed hydrolysis of Eucalyptus globulus wood. Bioresource Technology 109: 77-85

IV. Gütsch, J.S., Sixta, H. (2012) Regeneration of spent activated charcoals used for lignin removal from prehydrolysis-kraft prehydrolyzates, Industrial and Engineering Chemistry Research 51: 8624−8630

V. Gehmayr, V., Gütsch, J., Leschinsky, M., Zuckerstätter, G., Sixta, H. (2010) New aspects of residual lignin isolation. Holzforschung 64: 417-420

and the following patent application:

VI. Gütsch, J., Leschinsky, M., Sixta, H. (2010) Process for improved processability of hydrothermolyzates of lignocellulosic material WO2011/150436 A1

Contributions of the author:

Papers I - IV:	Experiments, analysis, first version of manuscript.
Paper V:	Experiments in part, manuscript in part.
Patent application VI:	Experiments, analysis, first version of application.

Other relevant publications and conference presentations not included in this thesis:

1. Gütsch, J.S., Sixta, H. (2011) Solution to the problem of lignin precipitation after autohydrolysis: HiTAC-Process (High Temperature Adsorption on Activated Charcoal). In: The third Nordic Wood Biorefinery Conference, Stockholm, Sweden. pp. 86-91
2. Gütsch, J.S., Sixta, H. (2011) Effect of activated charcoals on lignin and carbohydrates in solution. In: 241st American Chemical Society National Meeting and Exposition, Anaheim, California.
3. Gütsch, J.S., Sixta, H. (2011) Prehydrolysis of wood for xylooligomer extraction. In: 14th Austrian Chemistry Days, Linz, Austria.
4. Sixta, H., Borrega, M., Testova, L., Costabel, L., Alekhina, M., Guetsch, J. (2011) Progress and challenges in the separation and purification of xylan from hardwood. In: The third Nordic Wood Biorefinery Conference, Stockholm, Sweden.
5. Sixta, H., Guetsch, J., Nousiainen, T., Wollboldt, P. (2011) Progress and challenges in the isolation of xylan from eucalyptus wood. In: 5th International Colloquium on Eucalyptus Pulp, Porto Seguro, Bahia, Brazil.
6. Gütsch, J.S., Sixta, H. (2010) Vorhydrolyse: Abtrennung der lignin-stämmigen Fraktion. In: Tagungsband 6. Minisymposium Verfahrenstechnik, IFA Tulln, Austria. pp. 46-51
7. Gütsch, J.S., Sixta, H. (2010) Purification of *Eucalyptus globulus* water prehydrolysates. In: Proceedings 11th European Workshop on Lignocellulosics and Pulp, Hamburg, Germany. pp. 267-270

Contents

1 Objectives

The prehydrolysis-kraft process is a well established process for the production of dissolving pulps. During the first step, the prehydrolysis or autohydrolysis, hemicelluloses are dissolved that are hardly degraded in the following alkaline kraft cooking step. To date, the resulting hemicellulosic fraction is not used as a product due to lignin dissolution and precipitation that causes severe plugging of the equipment. Instead, the autohydrolyzates are neutralized with cooking liquor and burnt in the evaporation plant. This approach, however, leads to the destruction of valuable hemicellulosic components and raises the load of the recovery boiler.

In the present work, strategies for lignin reduction and removal from the hydrolyzates are presented in order to efficiently utilize the hemicellulosic fraction.

An objective of the following work was to evaluate the possibility to reduce the amount of lignin in the hydrolyzates by acid catalysis of the prehydrolysis reaction. Due to the higher acidity, the proportion of monosugars and thus the released amount of acetic acid were higher as compared to autohydrolysis conditions. Moreover, the amount of insoluble lignin particles in the hydrolyzate was reduced by acid catalysis, but still major amounts of soluble and insoluble lignin in the hydrolyzate would hinder the recovery of valuable hemicelluloses.

Therefore various purification methods were tested in order to remove the lignin, preferably at autohydrolysis temperature. The adsorption of lignin components on activated charcoals turned out to be selective and efficient, especially directly after the hydrolysis reaction at temperatures of 170 °C.

A cost effective regeneration process for the spent activated charcoals will be necessary for a commercial realization of the adsorption process. Therefore, desorption of lignin from the charcoal as well as thermal regeneration of the charcoals was examined in order to develop an appropriate recycling strategy for the exhausted charcoals.

2 Background

2.1 Prehydrolysis reactions

The term prehydrolysis describes an acid induced hydrolysis of oligomeric and monomeric sugars in plant biomass prior to a pulping step (Kraft, Sulfite) in order to dissolve hemicelluloses and render the lignin more reactive and the cellulose more susceptible to further chemical pulping. Thus, all three main wood components (lignin, hemicellulose and cellulose) undergo complex reactions in the course of prehydrolysis, which will be discussed in more detail in this chapter.

Reactions of Cellulose

Cellulose is the most abundant biopolymer on earth. Biologically, it is the structural component of the primary cell wall of green plants. Chemically cellulose is a linear polysaccharide consisting of $\beta(1\rightarrow4)$ linked D-glucose units. Hydrolysis is one of the major degradation mechanisms of polysaccharides, where the glucosidic bond between the sugar molecules is cleaved. Hydrolysis of cellulose can follow three possible pathways (Figure 1):

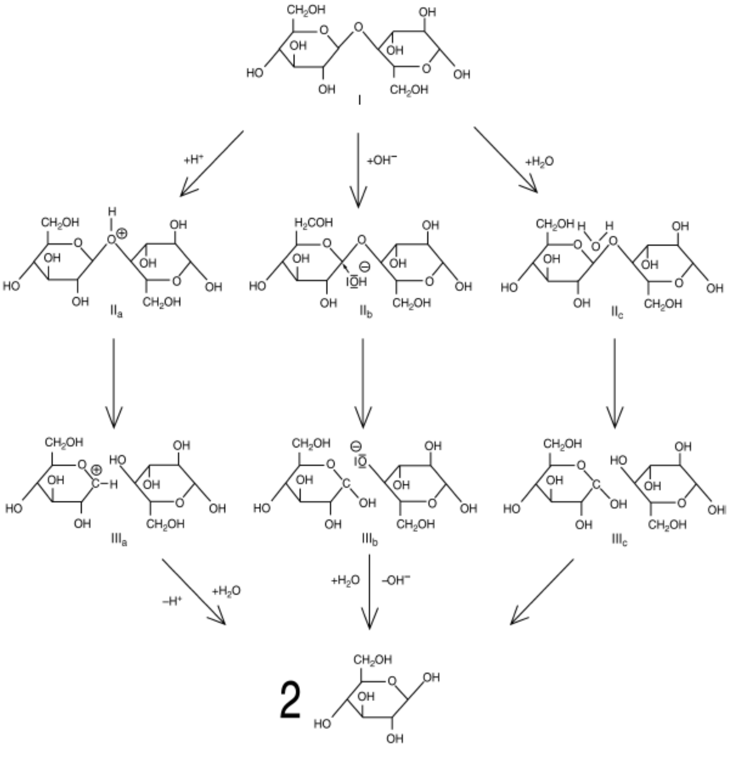

Figure 1: Hydrolysis of cellobiose. Acid (H^+ and index a), alkaline (OH^- and index b), and water catalyzed (H_2O and index c) hydrolysis (Bobleter 2005).

During acid hydrolysis a conjugated acid is formed which induces the glycosidic bond cleavage. Alkaline hydrolysis proceeds via the attack of the hydroxyl ion at the anomeric carbon atom. During hydrothermal cleavage H_2O adsorbs and water and glycosidic bond split simultaneously (Bobleter 2005).

Hydrolysis of cellulose leads to cellooligomers and subsequently to glucose monomers. Dehydration leads to the formation of hydroxymethylfurfural (HMF). Further complex side reactions of all intermediate products occur during the acid catalyzed hydrolysis. Minor amounts of glucose react to levoglucosan, isomaltose, or gentiobiose. HMF further reacts to levulinic and acetic acid. Insoluble humins are formed due to degradation reactions of both glucose and HMF (Girisuta et al. 2007). The occurrence of this multitude of side reactions demands a rather complicated approach for kinetic modeling of cellulose degradation during prehydrolysis, which is shown in Figure 2.

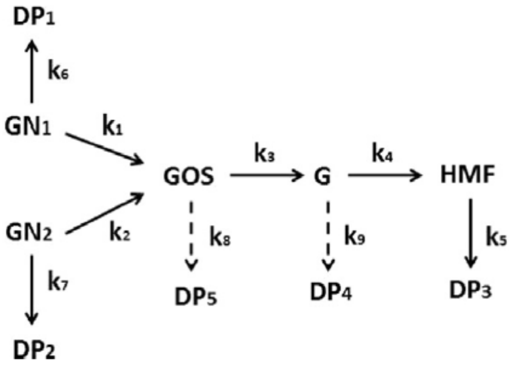

Figure 2: Kinetic model of glucan degradation during autohydrolysis. GN_1 rapid reacting glucan, GN_2 slow reacting glucan, GOS glucooligomers, G glucose, $DP_{1\text{-}5}$ degradation products (Borrega et al. 2011).

Reaction kinetics of glucan hydrolysis are accurately modeled as a series of consecutive first order reactions, where all intermediate molecules react to secondary degradation products (Borrega et al. 2011). Within this model, it is assumed that two cellulose fractions, fast (GN_1) and slow (GN_2) reacting cellulose (5 and 95 %, respectively), both degrade to glucooligosaccharides and subsequently to monomeric glucose and hydroxymethylfurfural. The rate constants of cellulose degradation reactions are rather small as compared to xylan degradation during autohydrolysis owing to two effects: the high crystallinity and the inaccessibility of cellulose (Deguchi et al. 2008) and the higher stability of glucosidic bonds of hexoses as compared to pentoses (Harris 1975). The degradation rates increase considerably with increasing temperature and hydrogen ions concentration (Qi et al. 2008). At high temperatures the transformation of crystalline cellulose to amorphous cellulose is reported, which leads to immediate hydrolysis and dissolution of the polysaccharide (Deguchi et al. 2008).

Reactions of Hemicellulose

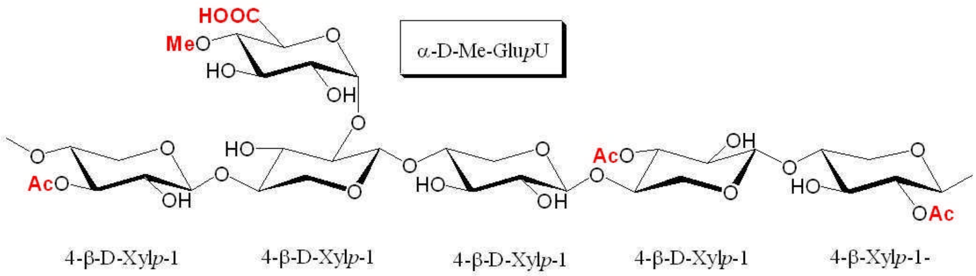

Figure 3: Stereochemical structure of an *O*-acetyl-*4*-*O*-methylglucurono-xylan.

Hemicelluloses are heteropolysaccharides. In hardwoods, the most abundant hemicelluloses are *O*-acetyl-4-*O*-methylglucurono-xylans, simply referred to as xylan (Figure 3). Depending on the hardwood species, the xylan content of wood ranges between 15 and 30 %. Xylan consists of a backbone of *β*(1→4) linked *D*-xylose units, where acetyl and 4-*O*-methyl-glucuronic acid groups are attached. Native xylan in beech and birch wood has an average degree of polymerization (DP) of 80 xylose units. The amount of acetyl- and 4-*O*-methyl-glucuronic acid groups per xylose unit varies upon origin and constitutes mean values of 7 and 1 per 10 xylose units in native wood, respectively (Sjöström 1981). In contrast to glucosidic bonds in cellulose, xylosidic bonds in xylan are easily hydrolyzed in acidic media and oligomeric and monomeric xylose units are formed. At prehydrolysis conditions, the acetyl groups are cleaved from the xylan backbone, yielding free acetic acid that acts as acid catalyst during prehydrolysis directly at the place of its release.

Acetyl groups in wood decrease drastically in the course of prehydrolysis, as hemicelluloses with attached acetyl groups are solubilized. Due to hydrolytic cleavage of acetyl groups, free acetic acid in the hydrolyzates then increases steadily with increasing hydrolysis intensity (Figure 4) (Leschinsky et al. 2009).

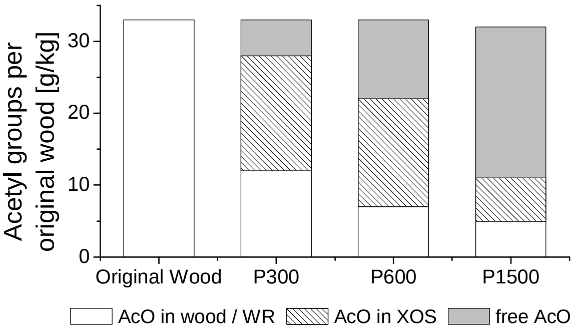

Figure 4: Mass balances of the acetyl groups (Leschinsky et al. 2009)

Methylglucuronic acid was found to stabilize xylan and thus to protect xylan from hydrolytic degradation (Conner 1984; Springer and Zoch 1968). Methylglucuronic acid itself is degraded during hydrolysis (Korte et al. 1991; Tunc and van Heiningen 2008) most probably due to decarboxylation reactions (Leschinsky et al. 2009; Nanji et al. 1925). These reactions are enhanced in an acid environment (Anderson et al. 1961).

In the secondary cell wall of hardwoods, a non-branched xylan that is associated with the cellulose and a branched xylan associated with lignin exist (Dammströmm et al. 2009). Depending on its association, xylan hydrolyses at different reaction rates. Xylan hydrolysis can be modeled according to the following reaction scheme assuming a sequence of first-order reactions (Borrega et al. 2011):

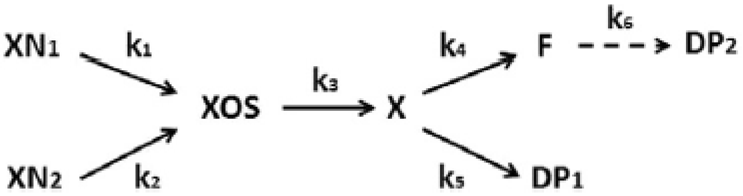

Figure 5: Reaction scheme of xylan hydrolysis. XN_1 and XN_2 are the rapid and slow degrading xylan fractions in wood, XOS, X, F, DP_{1-2} are xylooligomers, xylose, furfural and degradation products in the hydrolyzates.

Based on the two xylan types, Chen et al. (2010) proposed following mechanism for the xylan removal from the wood matrix during prehydrolysis: hydronium ions catalyze the hydrolysis of glucosidic bonds in xylan and lead to xylooligosaccharides (XOS) and xylopolysaccharides of a lower degree of polymerization (DP). When the DP of the xylans falls below 25, they become soluble and dissolve in the aqueous phase. Because hydrolysis is a random process, it takes some time until significant amounts of XOS are found in the hydrolyzates. This gives an increase in xylan dissolution rate with time. When the fraction of easily dissolved xylan is dissolved, hydrolysis rate decreases again due to the slower hydrolysis of xylan that is attached to lignin. During water prehydrolysis the subsequent reaction to XOS is rather slow. Thus, hemicelluloses are liberated as oligomers which are degraded to less substituted oligosaccharides of lower molar mass, further degradation to monomeric sugars is only observed with increasing treatment intensity (Testova et al. 2011). This consecutive reaction is considerably accelerated during sulfuric acid catalyzed hydrolysis (Parajó et al. 1994). The subsequent reaction to furfural (Figure 6) only gets pronounced at temperatures exceeding 170 °C (Zeitsch 2000).

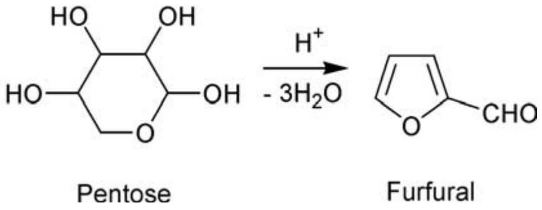

Figure 6: Dehydration of a pentose to furfural.

Reactions of Lignin

Depending on the acidity of the reaction media lignin undergoes a series of cleavage and condensation reactions. At neutral and weakly acidic conditions, homolytic cleavage of β-ethers in lignin occurs (reaction route C, Figure 7). With increasing acidity, acidolytic cleavage of β-ethers via benzylic carbocations (reaction routes A and B, Figure 7) can be expected (Li and Lundquist 2000). The parallel occurrence of lignin cleavage and condensation reactions at different rate constants during hydrolysis leads to a maximum of lignin solubility at a distinct treatment intensity (Lora and Wayman 1978b).

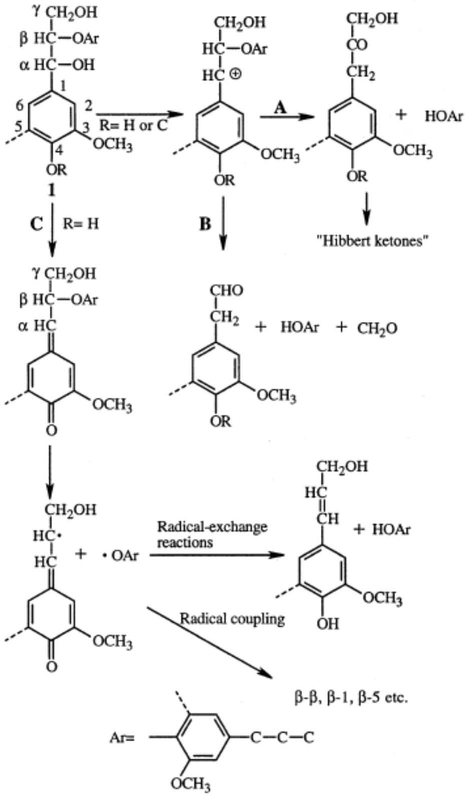

Figure 7: Reactions of lignin structures of the arylglycerol β-aryl ether type under acid and neutral conditions (Li and Lundquist 2000)

Cleavage of aryl-ether bonds results in the dissolution of lignin during prehydrolysis, and therefore in an increased phenolic hydroxyl group content and in a reduced amount of β-*O*-4 bonds in both the wood residue lignin and the lignin in the prehydrolyzate (Figure 8) (Leschinsky et al. 2008a). With increasing autohydrolysis intensity, the molecular weight of lignin decreases in all fractions. Thus, the amount of low molecular weight lignin which is soluble in the hydrolyzate increases with reaction time. Parallel the reactivity of lignin to acid-catalyzed re-condensation increases. Soluble lignin in the hydrolyzate tends to undergo acid catalyzed condensation reactions that lead to sticky precipitates of high molecular weight especially after cooling (Leschinsky et al. 2008b).

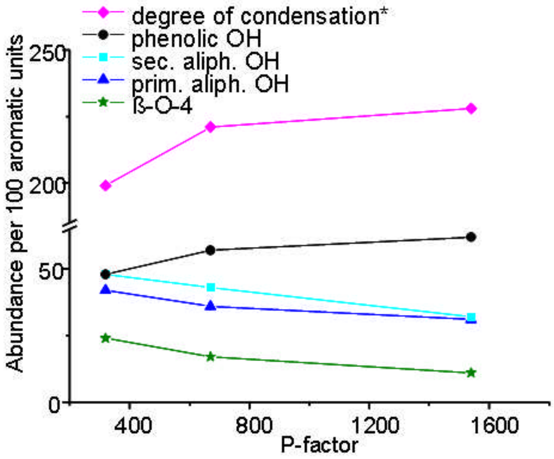

Figure 8: Development of lignin bonds and hydroxyl-groups with increasing hydrolysis intensity (Leschinsky et al. 2008a)

The formation of these precipitates can be hardly avoided. However, shorter prehydrolysis times and lower temperatures reduce the amount of lignin in the hydrolyzate. A high lignin content in the hydrolyzate causes major difficulties in the recovery of carbohydrate components because of precipitation and the formation of incrustations. A drastic decrease of precipitated lignin was only observed when SO_2 was added as acid catalyst, owing to the sulfonation of the lignin. Due to sulfonation the solubility of lignin increased significantly, yielding high amounts of lignosulfonates in the prehydrolyzates, thus counteracting to the intended selectivity of prehydrolysis (Leschinsky 2009).

Intensity of prehydrolysis

The intensity of autohydrolysis of *Eucalyptus globulus* wood chips is conveniently expressed as P-factor using an Arrhenius-type expression. An activation energy of 125.6 kJ mol^{-1} for the fast-reacting xylan (X_F) has been suggested for the P-factor (P_{X_F}) calculation in a prehydrolysis kraft pulp mill, based on extensive investigations of xylan hydrolysis from *Eucalyptus saligna* (Sixta 2006):

$$P_{X_F} = \int_{t_0}^{t} exp\left(40.48 - \frac{15106}{T}\right) dt \qquad (1)$$

where t is the residence time in minutes and T the reaction temperature measured in °C. Overend and Chornet (1987) introduced the severity factor R_0 to quantify the intensity of hydrothermal biomass treatment using the following expression:

$$R_0 = t \cdot \exp\left(\frac{T-100}{14.75}\right) \qquad (2)$$

where t is the residence time in minutes and T the reaction temperature measured in °C. The logarithmic plot of R_0 allows the illustration of the data in a more condensed form. To account for the addition of catalysts such as sulfuric acid and oxalic acid in equation (2) the initial proton concentration in the pre-treatment was considered according to equation (3) (Abatzoglou et al. 1992):

$$R'_0 = R_0 \cdot [H^+] = \log(R_0) - pH \qquad (3)$$

Until now, no approach has been found to describe autohydrolysis and acid catalyzed hydrolysis in one equation due to the two types of reaction taking place during both treatments to different extends: the hydrolytic and the acid catalyzed hydrolysis reaction.

2.2 Autohydrolyzate utilization

Prehydrolyzate composition

The composition of wood hydrolyzates depends on the wood source and the process conditions applied. The main components of the autohydrolyzates are oligomeric and monomeric xylose and lignin. Glucose, C_5-sugars other than xylan, furfural, HMF and acetic acid are present in minor amounts. At low prehydrolysis intensities only small quantities of carbohydrate derived products (<1.5 % at a P-factor of 70) are dissolved, but a substantial amount of lignin (Figure 9). With increasing intensity xylan dissolution reaches 15 % odw (oven dry wood), further hydrolysis of C_5-sugars leads to increasing amounts of monosugars and furfural. Decarboxylation reactions increase the amount of CO_2 in the gas phase and decrease the amount of carbohydrates in solution (Leschinsky et al. 2009). As described in chapter 2.1 acid catalyzed hydrolysis shifts the reaction equilibrium towards the monomeric sugars. Thus the product spectrum of acid catalyzed hydrolysis is significantly different (see also chapter 1 and chapter 4) and the range of application is confined to small molecules (monosugars, furfural, ethanol).

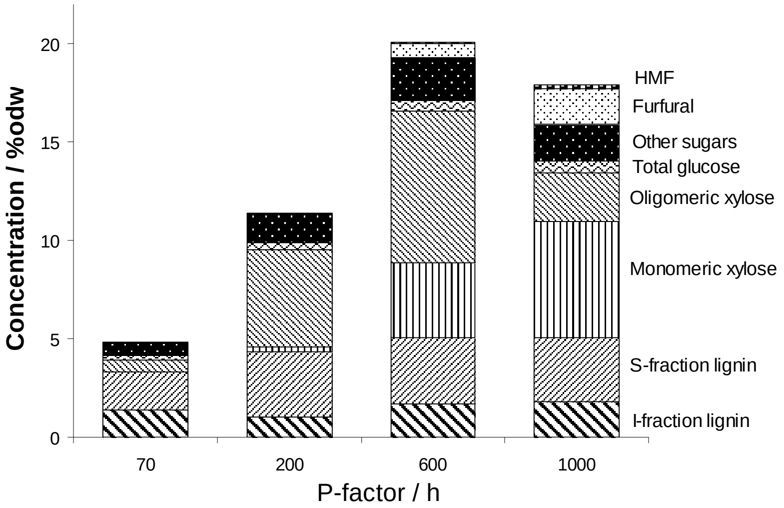

Figure 9: Composition of hydrolyzates at increasing prehydrolysis intensities (Paper III)

Prehydrolyzate Utilization

Efforts towards the utilization of the hemicellulosic fraction dissolved during prehydrolysis date back to the nineteen-thirties (Aronovsky and Gortner 1930). The UdSSR extensively used prehydrolysis technology of wood for the production of fodder yeast, ethanol and furfural (Aronovsky and Gortner 1930; Crönert 1987). However, after subsidies provided by the state ceased, most plants went into bankruptcy as they could not compete with plants using potatoes or grain as feedstock (Rabinovich 2009). Nevertheless, products derived from monomeric xylose add substantial profit when hydrolysis is not conducted as a sole reaction but as an additional pretreatment step in pulping industry (van Heiningen 2006). Products derived from monomeric xylose include sweeteners like xylitol (Liu et al. 2009), bioethanol (Ma et al. 2012), biodiesel (Corma et al. 2012) and platform chemicals (Gallezot 2012; Liu et al. 2012) like butanol (Fond et al. 1986) and furfural (Chheda et al. 2007; Weingarten et al. 2010). Furfural as a platform chemical substitutes fossil petroleum based products for example in furan resins or polyamides (Figure 10) and is therefore highly interesting for a society in search of renewable bio-based materials.

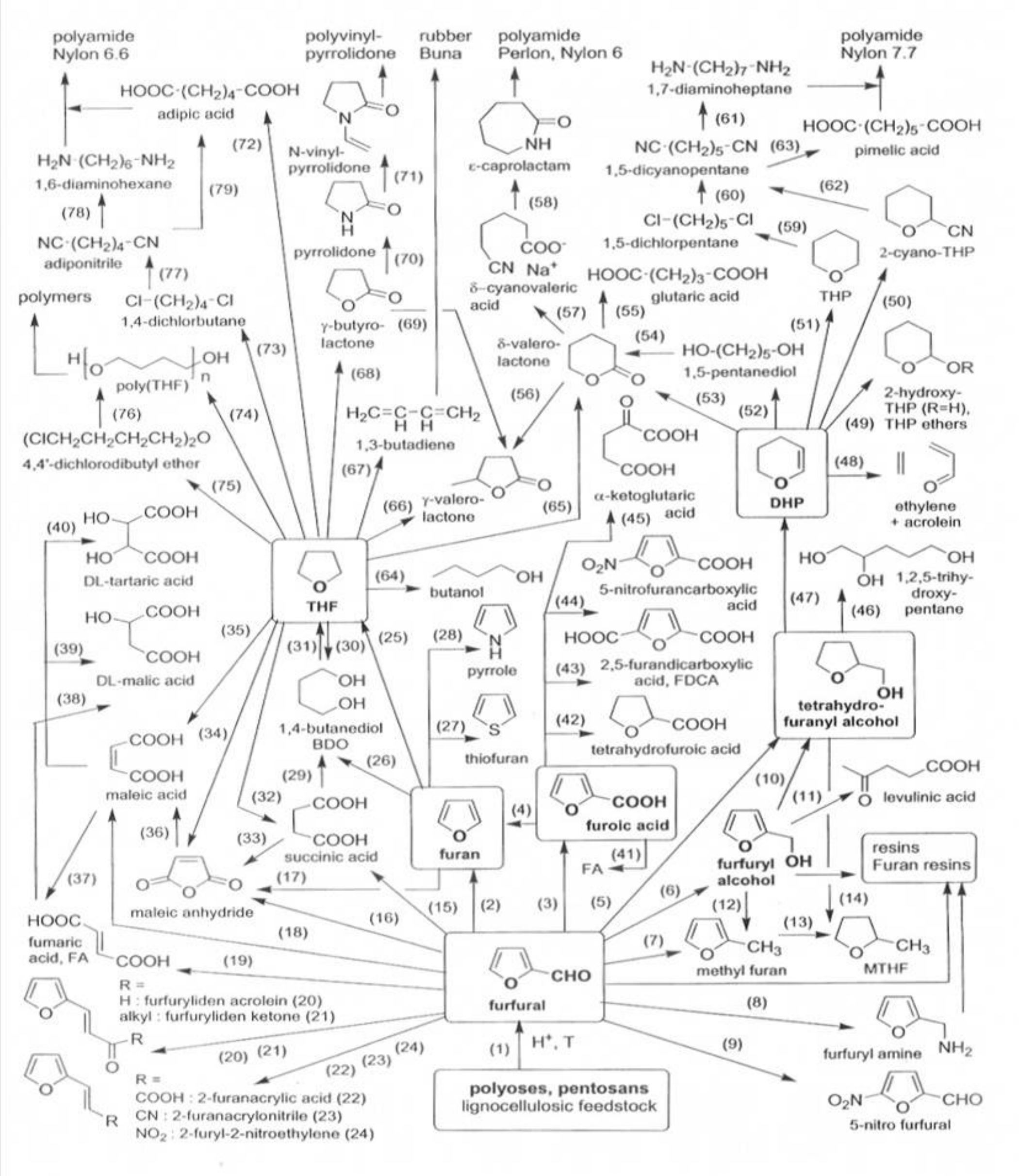

Figure 10: Furfural product tree (Kamm et al. 2008)

Starting in the year 2005 over 800 patents have been launched covering the topic of xylooligosaccharides. Depending on the molecular weight of the xylans and XOS and the distribution and type of side chains, xylans have found various areas of applications. High molecular mass xylan is used for improved mechanical properties of paper pulps and improved printability (Schroeder 2006). Furthermore, it was shown that the yield of paper pulps can be increased by the addition of xylan (Liu et al. 2011; Schild et al. 2010). Food industry uses the prebiotic properties of xylans in dietary supplements (Delcour et al. 2006). Prebiotic substances are generally indigestible by humans but favor the growth of enterobacteria and therefore promote the balance of the intestinal flora. Viscosity and structure properties of food products can be adjusted by using xylans, which leads to a better mouthfeel (Vaslin et al. 2002; Zhou 2004). Xylan films are utilized for biodegradable food packaging (Li et al. 2009; Mikkonen et al. 2009) and encapsulation of active ingredients (Serizawa 2009). In cosmetics xylan finds application in hair care and anti-aging products (Baik et al. 2007; Tanaka and Azumi 2005). A highly interesting and highly profitable field is the application of xylan, xylooligosaccharides and xylobiose in pharmaceutical products (Moure et al. 2006). The application range includes xylan as a matrix for drug delivery (Peng et al. 2011) for example in nasal sprays, drugs against gastro-intestinal diseases and high value preparations for cancer therapy (Melo-Silveira et al. 2012).

2.3 Prehydrolysis-kraft pulping

Prehydrolysis is applied prior to kraft cooking as it dissolves hemicelluloses that are hardly degraded in the following alkaline kraft cooking step. Thus the prehydrolysis kraft process yields high purity dissolving pulps for example for the manufacture of viscose fibers (Sixta 2006).

The alkaline kraft process is the world’s most abundant chemical pulping process and contributes to 90 % of the world’s chemical pulp production (Sixta 2006). Other alkaline pulping processes, like the soda-process and the soda-AQ process, only play a minor role. However, the selective soda-AQ process has high potential as a future sulfur-free eco-friendly pulping alternative (Schild et al. 2010).

The main active chemicals in alkaline kraft cooking are hydroxide and hydrosulfide anions. The hydrosulfide ion accelerates delignification and renders the nonselective soda cooking into a selective delignification process. Alkaline pulping processes, however, are not capable of selectively removing hemicelluloses for the production of high-purity dissolving pulps (Sixta 2006), because of the high resistance of hemicelluloses to alkaline degradation. Multistage kraft pulping processes comprise modifications before and after cooking to solubilize the hemicelluloses of the wood efficiently (Korteläinen and Backlund 1985; Sixta 2009). Typical modifications prior cooking are extraction steps with hot water (= prehydrolysis, autohydrolysis, hydrothermolysis) or dilute acids that were discussed in chapter 2.1.

Due to the lignin scaling problems (chapter 2.1) the state-of-the-art technologies for dissolving pulp production, VisBatch® and VisCBC®, use vapor phase prehydrolysis (Wizani et al. 1994). The prehydrolysis products are immediately neutralized and displaced with cooking liquor, which is also energetically favorable, as only one heating phase of the chips is necessary. Prehydrolysis by-products can, however, not be utilized using this technology.

Compared to kraft paper pulps, prehydrolysis kraft paper pulps show lower intrinsic fiber strength and fiber bonding quality, due to the lack of hemicelluloses (Santos et al. 2008; Schild et al. 2010). The low hemicellulose content, however, is a target value for dissolving pulp production. In comparison to acid sulfite cooking for dissolving pulp production the prehydrolysis kraft process leads to higher pulp purities at similar yield levels and to drastically reduced cooking cycle times (Sixta and Borgards 1999). A certain yield disadvantage of prehydrolysis kraft pulps is reported as compared to kraft pulps that are subjected to a cold caustic extraction step for hemicellulose removal, because prehydrolysis cleaves glycosidic bonds and thus cellulose is further degraded during the kraft cooking step (Schild and Sixta 2011). Prehydrolysis kraft pulps show a narrower molecular weight distribution than sulfite pulps which is also favorable for dissolving pulp applications (Sixta and Borgards 1999).

2.4 Lignin removal from autohydrolyzates

A high content of reactive lignin in soluble wood prehydrolyzates causes major difficulties in the recovery of xylooligosaccharides and xylose because of precipitation and the formation of incrustations. A large variety of purification methods has already been studied in order to eliminate lignin in the hydrolyzates, including mechanical, physical and chemical separation technologies. A list of processes described in literature is given in Table 1 and Table 2 (page 17 and 18). Most of these process steps are applied at room temperature, where part of the lignin already precipitated and the formation of incrustations is already expected in industrial scale processes. In most literature citations multiple process steps are applied in order to remove inhibitors or purify the product. Centrifugation, filtration, neutralization, overliming and even adsorption on charcoal are widely used as pretreatments prior to the “real” purification step, but the effect of such pretreatments is seldom monitored and quantified.

Physical separation

In recent years, nano- and ultrafiltration processes have found increasing interest for the purification of xylooligosaccharides. Monomeric sugars are rather easily separated from the oligomeric sugars (Al Manasrah et al. 2011; Gullon et al. 2008). Lignin, however, shows low retention and thus cannot be fully removed. Ultra- and nanofiltration processes suffer serious fouling of the membranes, due to pore blocking (Gullon et al. 2008). The fouling layer is composed of lignin, wood extractives (mainly fatty and resin acids) and hemicelluloses (Kallioinen et al. 2011). Thus, before entering membrane separation, an additional pretreatment for the removal of lignin is essential (Schwartz and Lawoko 2010). Gullon et al. (2008) therefore used centrifugation and dead-end filtration. Centrifugation of autohydrolyzates removed a large lignin fraction, but lignin was still found in all hemicellulosic fractions recovered (Tunc and van Heiningen 2011). Some of the lignin could be attributed to lignin-carbohydrate linkages.

Organic solvent extraction

Organic solvent extraction fulfills two purposes: First the purification of the carbohydrate solution for further fermentative use, second the extraction of lignin compounds for the production of lignin related products, e.g. dietary supplements with antioxidant activity (Cruz et al. 1999). Solvent extraction mostly aims at the extraction of phenolic components. Depending on the polarity of the solvent and the p*H* of the solution, furfural, HMF and acetic acid are removed in addition to lignin. The inverse process, where the carbohydrates are extracted from hydrolysis liquors using boronic acid carriers, is also reported (Griffin and Shu 2004).

Flocculation

For the flocculation of lignin from hydrolysis liquors, the addition of chitosan and PEO was tested, which showed minor flocculation efficiency (Saeed et al. 2011; Shi et al. 2011). The addition of cationic polymers, however, led to substantial lignin flocculation by charge neutralization and bridging effects (Kholkin et al. 1999).

Clarification using protein-rich sources

Polyphenols, like tannins, in wine and fruit juices cause high turbidity and sometimes even precipitation. Therefore, different technologies for the purification of these liquors are known. Due to the similarities between lignin and other polyphenols, the purification strategies in juice industry might also be applicable for prehydrolyzate treatments. Beside classical adsorption processes (e.g. with bentonite or silica sol) fruit juice industry uses protein rich sources for clarification (Oszmianski and Wojdyło 2007). Proteins build complexes with tannins and can be separated by sedimentation or the like. The ability of tannins to form insoluble complexes with proteins thereby increases with the molecular weight of the tannins and with an increasing number of *o*-dihydroxy phenolic groups (Wakayama and Lee 1987). The formation of protein-tannin complexes is also known from animal digestion where it inhibits feeding (Giner-Chavez et al. 1997; Marks et al. 1987). At the acid pH of the wood hydrolyzate most proteins denature, which might lead to an incorporated flocculation of lignins and proteins.

Adsorption

Adsorbent materials, such as non-ionic polymeric resins and activated charcoals, have proven to be applicable for the removal of lignin and sugar degradation products from carbohydrate containing liquors (Parajó et al. 1996b). Polymeric resins showed good efficiency in lignin removal, although they were not utterly selective as large amounts of carbohydrates (48 %) were adsorbed, too. 90 % of the xylose could, however, be recovered from the resin by water washing (Schwartz and Lawoko 2010).

An interesting utilization of hydrolysis lignin – the residue from total sulfuric acid hydrolysis of lignocellulosic biomass – is its application as lignin adsorbent. 53 % of lignin could be removed from the hydrolyzate which led to a fermentation yield increase of 500 % as compared to an untreated hydrolyzate (Björklund et al. 2002). Activated charcoals are widely used for the removal of furfural, HMF, acetic acid and lignin from hydrolysis liquors. The efficiency and selectivity of the process, however, varies greatly in literature, with maximum values for lignin removal of 95 % (Carvalho et al. 2006). The absolute capacity of an activated charcoal is generally characterized by its specific surface area and the distribution of pores on the charcoal surface. The role of micro- and mesopores of the activated charcoal on lignin adsorption is still under discussion. Montané et al. (2006) observed that the best selectivity toward lignin adsorption was provided by microporous charcoals with small mesopore diameters, a low number of mesopores, and a low concentration of basic surface groups, while Marton et al. (2006) found no significant difference between the charcoals investigated.

In general, adsorption of lignin on activated charcoals is highest at low p*H* values, a condition typically met in untreated autohydrolyzates (Venkata Mohan and Karthikeyan 1997). Nevertheless, a neutralization step is often applied prior to adsorption, as neutral p*H* is required for subsequent fermentative treatments. In addition to neutralization, filtration and evaporation stages are often proposed to remove volatile compounds and to purify the hydrolyzates before an adsorption step (Canilha et al. 2004; Parajó et al. 1996a; Sepúlveda-Huerta et al. 2006; Villarreal et al. 2006).

However, it is strongly recommended to remove the sticky and reactive lignin prior to the application of additional treatment steps, because lignin inevitably hampers the treatment by continuous precipitation.

Table 1: Methods for the purification of lignocellulosic hydrolyzates part I

Purification principle	Purification Agent	Purpose	Substrate	Max lignin removal*	Reference
Centrifugation	-	Removal of solid condensation products	Hardwood autohydrolyzate	27 %	(Leschinsky et al. 2008a; Tunc and van Heiningen 2008)
Overliming	Calcium hydroxide	Neutralization, improved fermentation, xylose crystallization	H_2SO_4 hydrolyzate	26 %	(Frazer and McCaskey 1989; Griffin and Shu 2004; Han et al. 2006; Kholkin et al. 1999; Khristov et al. 1989; Marton et al. 2006; Parajó et al. 1996a)
	Calcium hydroxide	Neutralization, improved fermentation	Hardwood autohydrolyzate	n.d.	(Khandelwal et al. 1980; Mendes et al. 2009)
	Calcium hydroxide, Sodium Sulfite	Neutralization, improved fermentation	Hardwood H_2SO_4 hydrolyzate and autohydrolyzate	60 %	(Converti et al. 2000)
Organic solvent extraction	Trichloroethylene, benzene, chloroform, hexane, diethyl ether, ethyl acetate	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	84 %	(Cruz et al. 1999; Frazer and McCaskey 1989)
	Diethyl ether, methylpropyl ether, di-isopropyl ether, methylene chloride, chloroform, methylethyl ketone, methyl isobutyl ketone	Detoxification	Lignocellulosic acid hydrolyzate	n.a.	(Hess et al. 1965)
	Ethyl acetate, Ethanol, acetone, 2-propanol	XOS purification	Hardwood autohydrolyzate	n.a.	(Vázquez et al. 2005; Vázquez et al. 2007)
	Trialkylamine, n-octanol, kerosene	Improved fermentation	Corn straw H_2SO_4 hydrolyzate	n.a.	(Yu et al. 2009)
Selective extraction of sugars	Boronic acid carriers in organic solution	Purification and concentration of sugars	Bagasse H_2SO_4 hydrolyzate	> 90 %	(Griffin and Shu 2004)
Ion exchange	Cation exchange resins	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	15 % (Frazer)	(Carvalho et al. 2006; Frazer and McCaskey 1989)
	Anion exchange resins	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	53 %	(Frazer and McCaskey 1989)
	Anion exchange resins	XOS purification	Hardwood autohydrolyzate	n.d.	(Vázquez et al. 2007)
	Anion exchange resin + membrane	Acetic acid removal	Corn-Stover H_2SO_4 hydrolyzate	n.a.	(Han et al. 2006)
	Combination of cation and anion exchange resins	Xylose crystallization	Hardwood Prehydrolyzate before and after posthydrolysis	Canilha n.d. 95 % (Kristov)	(Canilha et al. 2004; Khristov et al. 1989; Mozolová et al. 1977)
	Combination of cation and anion exchange resins	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	93 %	(Villarreal et al. 2006)
Chromatographic separation	Dowex99, PVP	Purification of sugars	Corn-Stover H_2SO_4 hydrolyzate	n.d.	(Xie et al. 2005)

* maximum values of all literature cited are given, spreading of values is high.

Table 2: Methods for the purification of lignocellulosic hydrolyzates, part II

Purification principle	Purification Agent	Purpose	Substrate	Max lignin removal	Reference
Adsorption	Non ionic polymeric adsorbent	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	72 % (Frazer)	(Carvalho et al. 2006; Frazer and McCaskey 1989)
	Non ionic polymeric adsorbent	Removal of lignin	Hardwood H_2SO_4 hydrolyzed autohydrolyzates	91 % (48 %reduction of xylose)	(Schwartz and Lawoko 2010)
	Diatomaceous earths	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	< 50 %	(Carvalho et al. 2006)
	Activated charcoals	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	95 % (drastic xylose losses observed)	(Carvalho et al. 2006; Converti et al. 2000; Frazer and McCaskey 1989; Parajó et al. 1998)
	Activated charcoals	Acetic acid removal	Sugar cane bagasse H_2SO_4 hydrolyzate	n.d.	(Marton et al. 2006)
	Activated charcoals	Improved fermentation	Rice straw H_2SO_4 hydrolyzate		(Mussatto and Roberto 2004)
	Activated charcoals	Soluble lignin removal	Hardwood H_2SO_4 hydrolyzate	88 % (45 % reduction of XOS)	(Montané et al. 2006; Parajó et al. 1996a; Parajó et al. 1996b)
	Activated charcoals	Removal of F, HMF, acetic acid, Improved fermentation	Hardwood autohydrolyzate	n.d.	(Lee et al. 2011)
	Activated charcoals	Soluble lignin removal	Autohydrolyzate of Almond shells	n.d.	(Mozolová et al. 1977)
	Activated charcoals	Improved fermentation	Straw H_2SO_4 hydrolyzate	n.d.	(Sepúlveda-Huerta et al. 2006)
	Lignin hydrolysis residue	Improved fermentation	Softwood H_2SO_4 hydrolyzate	52 %	(Björklund et al. 2002)
Flocculation	Cationic polymers	Removal of lignin-humic substances	Softwood H_2SO_4 hydrolyzate	> 90 %	(Kholkin et al. 1999)
	Anionic and cationic polymer	Improved fermentation	Wood H_2SO_4 hydrolyzate	n.d.	(Hughes and Symes 2006)
	Chitosan	Removal of organics	Autohydrolyzate	38 %	(Saeed et al. 2011)
	PEO	Lignin removal	Acidified neutralized hardwood autohydrolyzate	25 %	(Shi et al. 2011)
Vacuum evaporation	-	Improved fermentation	Hardwood H_2SO_4 hydrolyzate	No lignin removal	(Carvalho et al. 2006)
Filtration	Nanofiltration	Concentration and purification of XOS	Hardwood autohydrolyzate	< 59 %	(Amidon et al. 2008; Liu et al. 2008; Moure et al. 2006; Vegas et al. 2006)
	Ultrafiltration	Concentration and purification of XOS	Softwood autohydrolyzate	21 % lignin retention at 53 % xylan retention	(Al Manasrah et al. 2011; Kallioinen et al. 2011)
	Ultrafiltration	Purification of XOS	Almond shell autohydrolyzate	n.a.	(Nabarlatz et al. 2007)
	Ceramic ultra- and nanomembranes	Concentration and purification of XOS	Hardwood autohydrolyzate	n.a.	(Gullon et al. 2008)
	Ceramic microfilters	Removal of inhibitors	Hardwood autohydrolyzate	53 %	(Hasan et al. 2011)

Theory of adsorption isotherms

The adsorption equilibrium is a dynamic equilibrium that is dependent on the rate constants of adsorption and desorption, and thus on the temperature and the concentration of adsorbent and adsorbate. Depending on the strength of the interaction of adsorbent and adsorbate we can differentiate between physisorption, where only van der Waals forces contribute to the binding strength, and chemisorption, where the adsorbate is covalently linked to the adsorbent surface (Atkins 2002).

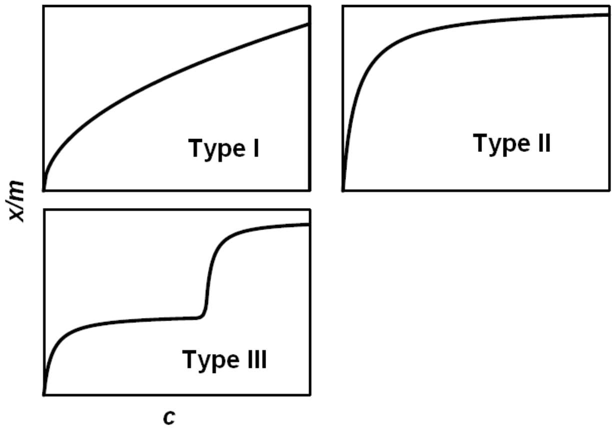

Figure 11: Types of adsorption isotherms. x/m concentration of adsorbate on surface, c equilibrium concentration in solution (Schlodder 2009)

A number of (mostly empirical) models have been developed for the description of adsorption isotherms. A Langmuir isotherm (Figure 11, Type II) describes adsorption in a monomolecular layer, where adsorption of a particle is independent of the degree of surface coverage according to the following equation (Langmuir 1932):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot \beta} + \frac{C_e}{Q_0} \qquad (4)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of adsorbate in solution (mg L^{-1}), Q_0 is the maximum adsorbate uptake per unit mass of adsorbent (mg g^{-1}), and β is the Langmuir constant (L mg^{-1}).

The Freundlich adsorption isotherm (Figure 11, Type I) additionally relates the concentration of the solute on the surface of the adsorbent, to the concentration of the solute in the liquid phase in a logarithmical relationship (Freundlich 1907).

The Freundlich equation can be written as:

$$q_e = k_f \cdot C_e^{1/n} \qquad (5)$$

where q_e and C_e are defined similar to the Langmuir terms, k_f is the Freundlich constant related to the adsorption capacity (mg g^{-1} (mg $L^{-1})^n$), and n is a dimensionless empirical parameter representing the heterogeneity of the surface.

Type III isotherms describe the formation of multilayers on the adsorbent surface. The most commonly used expression of this kind is the BET-isotherm developed by Brunauer, Emmet and Teller (Brunauer et al. 1938). Some simplifying assumptions were introduced in order to extend the Langmuir equation to multilayer adsorption: 1) physisorption is the only adsorption mechanism, 2) no interaction between the layers occurs and 3) the Langmuir theory can be applied to each single layer. The resulting BET-isotherm can be written as:

$$q_e = \frac{K Q_{\max} C_e}{(C_{sat} - C_e) \cdot (1 + \frac{(K-1)C_e}{C_{sat}})} \qquad (6)$$

where q_e and C_e are defined similar to the Langmuir terms, Q_{max} is the maximum adsorbate uptake in one layer, C_{sat} is the saturation concentration of the adsorbate, and K is the BET coefficient. The BET model is also widely-used for the calculation of the specific surface area of adsorbents by physical adsorption of gas molecules of a known size.

Modeling of hydrolyzate adsorption data with common adsorption isotherms

Lignin adsorption on activated charcoals at room temperature was moderately fitted by Freundlich isotherms (Montané et al. 2006; Parajó et al. 1996a) and also by Langmuir isotherms (Venkata Mohan and Karthikeyan 1997). The underlying reason to use the one or the other model, however, was not seriously discussed. Results of the Freundlich fit showed that the adsorption capacity and binding strength (expressed as Freundlich coefficient k_f) of lignin increased significantly with an increasing amount of acidic surface groups. Xylooligosaccharide adsorption capacity was solely enhanced with increasing mesopore volume (Montané et al. 2006). The temperature in the range of 20-60 °C had only minimal influence on the shape of lignin adsorption isotherms. Still, the binding strength was lower at higher temperatures (Parajó et al. 1996a). The influence of p*H* on the adsorption of lignin is rather contradictorily discussed in literature: while Parajó et al. (1996a) reported only minimal influence of the p*H* in the range from 3-7, Venkata Mohan and Karthikeyan (1997) observed 40 % less lignin adsorption when increasing the p*H* from 2 to 10.

2.5 Regeneration of spent activated charcoals

An idea of this thesis was to perform the adsorption of lignin directly after hydrolysis at hydrolysis temperature in order to prevent the lignin scaling problems. In industrial scale, it will be necessary to find a regeneration process for the spent activated charcoals in order to guarantee optimal economic efficiency.

Based on the fact that lignin is built of phenolic subunits - although highly macromolecular and therefore distinctly different in behavior - it was assumed that some processes for phenol desorption are applicable for prehydrolysis-lignin desorption from charcoal. In their review on the adsorption of phenolic compounds on activated charcoal Dabrowski et al. (2005) depict the influence of various process parameters on the adsorption behavior. These parameters include the type of activated charcoal, surface functionalities, p*H*, the oxygen availability and potential electrolyte addition. The inductive effect of methoxyl- and ethoxyl substituents leads to a strong binding of phenols to the charcoal matrix and to a high degree of irreversible adsorption (Dabrowski et al. 2005). Increasing temperature and adsorption time further enhances chemisorption of phenols and leads to polymerization reactions on the charcoal (Dabrowski et al. 2005). These effects are likely to occur when autohydrolysis lignin is adsorbed at high temperatures, because autohydrolysis lignin shows a high degree of methoxyl-groups (20 %) (Leschinsky et al. 2008a). Further interaction mechanisms described are donor-acceptor interactions between the aromatic ring and alkaline surface groups such as carbonyls, dispersion effects and electrostatic attraction (Busca et al. 2008).

Processes for phenol desorption include thermal desorption and solvent extraction (Soto et al. 2008; Taylor and Lester 1996), as well as microwave regeneration (Chang et al. 2010). Microwave regeneration utilizes the fact that charcoals have dielectric surface functionalities that absorb microwave energy and convert it to thermal energy. Anionic and cationic surfactants find application for the desorption of benzodiamine dyes in a process called surfactant enhanced carbon regeneration (SECR). The anionic tensides SDS (Sodium dodecyl sulfate) and AOT (Sodium 1,4-*bis*(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate) showed a considerably better performance than their cationic counterparts and led to a desorption of 40 – 65 % benzodiamine (Purkait et al. 2007). Solvent extraction with dichloromethane/methanol (93:7 v/v) at 140 °C was effective for the recovery of chlorinated phenols up to an efficiency of 75 %, although short desorption times (5 min) where applied due to the degradation of the products (Taylor and Lester 1996). Ethanol found application in the desorption of pomace from charcoal. Desorption efficiency, however, was only about 20 % (Soto et al. 2008).

If the desorption of matter is not efficient any more spent charcoals are either submitted to landfilling, burnt for energy generation or thermally regenerated. Thermal regeneration is performed in furnaces at tempera °C is more commonly used (Komori et al. 1975). Conventional oxygen free regeneration processes consist of a drying step at 105 °C, a pyrolysis step under inert atmosphere at temperatures of 650-850 °C, and an oxidation step with CO_2, steam, or a combination of both at 650-850 °C (Tarbert 2009). Steam is applied for the removal of volatile organic compounds and enhances regeneration in a way that treatment temperatures – and therefore costs – can be reduced significantly (Chestnutt et al. 2007). Regeneration of charcoal saturated with benzene and toluene is even possible at temperatures of only 250-350 °C in oxygen containing atmosphere. Generally, adjusting the oxygen content during the carbonization step is a plausible means to tailor the regenerated activated carbon. Regeneration efficiency is highly dependent from the type of charcoal, the adsorbed substances and the process chosen and can add up to 100 % (Carratalá-Abril et al. 2010).

The thermal regeneration step is similar to activated charcoal production. Traditional precursors for activated charcoal production are coal, coconut shells, lignite, wood and peat (Suhas et al. 2007). In recent years various other materials, including cellulose (Huang et al. 2001), hydrolysis lignin (Zou and Han 2001) and kraft lignin (Montané et al. 2005; Rodriguez-Mirasol et al. 1993) have been successfully tested for charcoal production. Thus a thermal regeneration step of a lignin loaded charcoal might yield an additional amount of charcoal due to the conversion of lignin to activated charcoal.

3 Materials and methods

3.1 Wood chips

Eucalyptus globulus wood was chosen for the experimental work in this thesis. It represents a fast growing wood species that shows good characteristics for pulping. Due to its homogenous morphological structure and its chemical composition which is characterized by high cellulose and low hemicellulose contents *Eucalyptus globulus* wood is particularly suited for the manufacture of dissolving pulps (Kordsachia et al. 1999). *Eucalyptus globulus* wood chips were kindly supplied by ENCE (Huelva, Spain). The trees grown in Uruguayan plantations were harvested at an age of 8-9 years. Before chipping, the logs were stored for 2-3 months. The chips were shipped to Huelva (Spain) where a sample was taken and sent to the Wood Kplus laboratories in Lenzing (Austria). In total, 3-4 months passed between harvesting the trees and freezing the chips in the laboratory. The chips were ground with a Retsch-type grinding mill and fractionated. The fraction with particle sizes between 2.5 and 3.5 mm was collected and used for the prehydrolysis experiments. The dry content of the wood chips (82.9 %) was measured after drying at 104 °C until constant weight (48 h). Analytical methods for wood composition evaluation are given in chapter 3.7. The native wood composition is given in Table 3.

Table 3: Composition of native wood

Wood component	% odw
Glucan	39.90
Xylan	14.90
Rhamnan	0.10
Arabinan	0.30
Mannan	0.40
Galactan	1.30
Klason lignin	23.60
Acid soluble lignin	4.80
Ash	0.32

3.2 Autohydrolysis and acid hydrolysis

Autohydrolysis was carried out in a lab-scale Parr reactor station with a reactor volume of 450 mL, mechanical stirring and temperature control. 50 g of wood were placed inside the reactor. Deionized water was added to achieve a liquor-to-wood ratio of 5:1. Catalysis with acids was performed in order to evaluate the effect of low temperatures and treatment times on lignin dissolution during prehydrolysis. Therefore, the acid catalysts sulfuric acid (0.01 – 0.1 M), oxalic acid (0.01 – 0.1 M) and acetic acid (0.02 – 0.15 M) were added, respectively. Sulfuric acid was used because it is classical hydrolysis catalyst which is widely described in literature and also used in industry mostly for total hydrolysis of biomass. Oxalic acid was chosen because it is an organic dicarboxylic acid which does not contain the environmentally unfavorable heteroatom sulfur and which is indicated in literature as suitable for biomass prehydrolysis. Acetic acid was chosen for comparison with autohydrolysis, as it is the actual catalyst during autohydrolysis. The reactor was heated up to reaction temperature (120-200 °C) within minimum heating time (ca. 30 min). The temperature was held until the desired prehydrolysis-factor (P-factor) or prehydrolysis time was reached. For autohydrolysis experiments the P-factor represents the intensity of the treatment. For acid hydrolysis experiments, models that also consider the acid strength of the reaction media were chosen (R_0 and R_0’). P-factor, R_0 and R_0’ were calculated from the recorded temperature/time data according to Sixta (2006), Overend and Chornet (1987) and Abatzoglou (1992), respectively, based on an activation energy for xylan hydrolysis of 125.6 kJ mol^{-1}. The prehydrolyzate was subsequently separated from the wood residue by displacement with nitrogen to a preheated second reactor saturated with steam at prehydrolysis temperature following the protocol of Leschinsky (2009). The isothermal phase separation recovered all components that were dissolved in the prehydrolyzate at prehydrolysis temperature, particularly the components that are insoluble at lower temperatures. During this separation step, no temperature and pressure drop occurred. In the case of prehydrolysis at 200 °C the second reactor was held at 170 °C in order to avoid extensive carbohydrate degradation. If not mentioned otherwise following prehydrolysis standard conditions were used:

Maximum reaction temperature:	170 °C
Reaction time:	60 min (≙ P-factor 600 h at 170 °C)

3.3 Hydrolyzate purification

Autohydrolysis lignin tends to form sticky precipitates with increasing processing time of the hydrolyzate at high temperatures. A certain processing duration, however, is inevitable in industry in order to recover the thermal energy of the hydrolyzates. Especially large heat exchanger surfaces are prone to incrustations. Therefore, we went for a purification method that is also applicable at high temperatures. Separation by centrifugation was excluded after preliminary tests showed insufficient efficiency. Filtration and membrane separation were not closely investigated due to the stickiness of the lignin and the fouling reported in literature. Possible high temperature separation methods were deduced from room temperature experiments.

Lignin removal at room temperature

A series of flocculants and adsorbents was screened for the removal of lignin from prehydrolyzates at room temperature (20 °C). The additives were chosen in order to cover a wide range of purification mechanisms, including classical adsorption on aluminium oxides, montmorillonites and activated charcoals; flocculation by charge neutralization and by bridging effects; and coflocculation with protein-rich sources as it is known from juice clarification.

Therefore prehydrolyzate was produced following the standard prehydrolysis protocol (170 °C, P-factor 600 h), isothermal liquid transfer and ice cooling. The additives were added in a series of concentrations to 5 mL autohydrolyzate, shaken on a Vortex shaker and stored at room temperature for 24 hours. Liquors where protein rich sources were added were filtered over a Whatman folded filter. Other additives were separated from the prehydrolyzate via vacuum filtration using a 0.45 µm membrane.

Information on the charcoals employed is listed in Table 4. Standard supermarket products were used for unskimmed milk, UHT-milk, soy milk, Maresi and egg white. Whey protein Fondolac 80 S, supplied by Meggle, was used after dissolution of 10 g in 250 mL deionized water, yielding in a turbid emulsion. Non-ionogenic surfactant Poro TS 5108 was purchased from Pointner & Rothschädl, Hansanyl OS A from Hansa GmbH. Aluminium oxides (WN6, neutral, activation grade super I and activated, neutral Brockmann I), montmorillonites (KSF and K-10), $Ca(OH)_2$ and molecular sieves were purchased from Sigma-Aldrich.

HiTAC-processing

The adsorption of lignin on activated charcoals proved to be an efficient and selective method for lignin removal at room temperature. Furthermore, charcoals show enough thermal stability for the adsorption of lignin also at prehydrolysis temperature. The adsorbtion characteristics on activated charcoals vary with their specific surface area, the surface functionalities and their pore size distribution. Therefore, a range of charcoals was tested for high temperature lignin adsorption.

For high temperature adsorption on activated charcoal (HiTAC) the setup described in chapter 3.2 was used. The activated charcoal (AC) was placed in the second reactor additionally to the water necessary for steam production for isothermal displacement. After displacement, the temperature in the second reactor was maintained until the required adsorption time was accomplished. After the adsorption, the reactor was immediately cooled down to below 40 °C with ice water. Adsorption time of 0 min represents the minimal adsorption time possible to record. The minimum adsorption time at 170 °C is estimated to be less than 2 min, followed by a cooling time to below 40° C of 10 - 15 min. The charcoal was separated from the prehydrolyzate via vacuum filtration using a 0.45 µm membrane. Information on the charcoals employed is listed in Table 4.

Table 4: BET surface area, pH and ash content of the activated charcoals.

Type of activated charcoal	**Producer**	**BET** / $m^2 g^{-1}$	**pH***	**Ash** / %
Carbopal Gn-AZ	Donaucarbon, Germany	1270	5.9	n.d.
Sigma decolorizing	Sigma-Aldrich, US	880	6.7	1.1
Norit®	Norit, Netherlands	560	6.0	12
HOC Super	Rheinbauer Brennstoff GmbH, Germany	280	11.2	8.7

* pH in water at a concentration of 50 g L^{-1}

If not mentioned differently, standard adsorption parameters were used as follows:

Adsorption temperature:	170 °C
Adsorption time:	20 min
Charcoal:	Sigma decolorizing

3.4 Regeneration of spent activated charcoals

High temperature adsorption of lignin on activated charcoals was very efficient in terms of lignin adsorption and selective towards carbohydrates. A reiterate utilization of the charcoals, however, was not possible due to a severe decrease in the specific surface area during adsorption, which necessitates ongoing regeneration of the charcoals for economic reasons. Two strategies were pursued for this purpose: solvent desorption of lignin and thermal regeneration of the spent charcoals. Solvent desorption would enable the utilization of the autohydrolysis lignin, a lignin free of sulfur, and would consume less energy than is needed for thermal regeneration.

Solvent desorption

Solvents, which are known for the dissolution of lignin, were used for the experiments. 1 g of spent activated carbon was subjected to 5 mL of solvent (0.5 N NaOH, acetone/ water 5:1 (v/v), ethanol, acetic acid, DMSO) and shook at room temperature overnight. AC was separated via a 0.45 µm filter and washed with 100 mL deionized water.

Thermal regeneration of charcoals

5 g of spent activated charcoal were weighed in a sagger and placed in a tube furnace. The furnace was heated under nitrogen (24 L h^{-1}) at a slope of 3 °C min^{-1} to the regeneration temperature (850 and 950 °C). Carbonization was performed at regeneration temperature for 30 and 45 min using carbon dioxide (24 L h^{-1}). Subsequently the charcoal was cooled under nitrogen (24 L h^{-1}) overnight. One regeneration experiment was performed using air as oxidizing agent. Therefore activated charcoal was heated in the furnace at a slope of 3 °C min^{-1} under air atmosphere to 300 °C. Temperature was held for 30 min, subsequently the charcoal was cooled under air overnight.

3.5 Xylan recovery

The hydrolyzate used for xylan isolation was produced according to chapter 3.2 and 3.3 (HiTAC-processing) using 5 g of activated charcoal for lignin adsorption. Adsorption time was set to 10 min. Xylan was precipitated from the filtrate by the addition of ethanol in a volumetric ratio of 8:1. After 48 h in the refrigerator the generated light grey precipitate was centrifuged and dissolved in water. Surplus ethanol was removed by rotary evaporation and xylan was finally freeze-dried.

3.6 Lignin isolation from pulp

Pulp

Eucalyptus globulus wood chips were subjected to soda-AQ continuous batch cooking (CBC) (Sixta 2006) in a 10 liter digester (H-factor 700, 94 min at T_{max} of 160 °C) with synthetic cooking liquor (30.9 g L^{-1} effective alkali, 0.2 % AQ on oven dry wood, alkali consumption 21 %).

Lignin isolation and purification

Soda-AQ pulp (kappa 14) was subjected to acetone extraction with a liquid-to-solid ratio (L/S) of 10. An optional alkaline extraction was performed (0.3 % NaOH, L/S 50, 1 h reflux, nitrogen atmosphere) and lignin was isolated via multi-step acidolysis (Evtuguin et al. 2001).

3.7 Analytical methods

Wood and wood residue

Klason lignin and acid soluble lignin of the wood chips and wood residues were measured according to Tappi T222om 98 (Tappi 1998).

The carbohydrate composition of all solid samples was investigated using high performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD) after a two-stage sulfuric acid total hydrolysis (Sixta et al. 2001). Furfural and hydroxymethylfurfural (HMF) which are formed during total hydrolysis (TH) from pentoses and hexoses were quantified and added to the results for xylose and glucose, respectively. Determinations by TH/HPAEC-PAD were performed at least twice.

Hydrolyzate

Lignin content was analyzed via UV/VIS-spectrometry (absorption coefficient of 110 L g^{-1} cm^{-1} at 205 nm according to Tappi um-250, (Tappi 1991). Furfural and HMF were quantified via HPLC on a Hypersil ODS column with UV detection at 277 nm with 14% (v/v) acetonitrile as eluent at a temperature of 65 °C. Acetic acid was determined via HPLC on a Rezex ROA column with refractive index (RI) and UV detection and 0.005 M H_2SO_4 as eluent at a temperature of 65 °C. Sugar monomers were determined by direct application of a HPAEC- PAD (Sixta et al. 2001). The total carbohydrate composition was analyzed via two-stage sulfuric acid TH with HPAEC-PAD. Furfural and HMF which are formed during TH from pentoses and hexoses, were quantified and added to the results for xylose and glucose, respectively. Determinations by TH/HPAEC-PAD were performed at least twice. The amount of sugar oligomers was calculated by subtracting the monomer content from the results determined after TH. Neutral xylooligosaccharides (XOS) were quantified by HPAEC-PAD up to a degree of polymerization (DP) of 6 (Griebl et al. 2006). XOS with a DP higher than 6 and acidic XOS could not be quantified due to a lack of commercially available standards, but where calculated as the difference between the sum of carbohydrates with a DP of 1-6 and the total amount of sugars determined after total hydrolysis. Size-exclusion chromatography (SEC) of the hydrolyzate was performed as described by Sixta et al. (2001) on two PSS MCX columns (1000 Å, 300*8 mm) with 0.5 M NaOH as mobile phase at a flow rate of 1 mL min^{-1}, RI and viscosimetric detection, allowing universal calibration. Calibration was carried out with a set of cello-oligomers and pullulan standards. Turbidity was measured on a Hach 2100P turbidimeter.

Xylan characterization

Degradation of hemicelluloses to products other than furfural as well as an incomplete cleavage of the methylglucuronic acid (MeGlcA) from the xylan backbone can result in imprecise results of carbohydrate analysis using TH. In addition, MeGlcA is degraded during conventional carbohydrate analysis using TH and cannot be determined. Acid methanolysis with GC-FID detection according to Sundberg et al. (1996) was therefore used in addition to TH/HPAEC for xylan characterization. This allowed the reliable quantification of neutral sugars and uronic acids. Carbohydrate determination using methanolysis with GC-FID were performed at least thrice. Acetyl groups of the xylans were determined as acetic acid measured by HPLC on a Rezex ROA column with RI and UV detection and 0.005 M H_2SO_4 as eluent at a temperature of 65°C subsequent to two stage sulfuric acid total hydrolysis. SEC was performed as described by Sixta et al. (2001)

Lignin Characterization

Elemental analyses were performed by the Fraunhofer IAP. Methoxy group content was measured according to the standard protocol of Vieböck and Schwappach (1930). FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer using golden gate attenuated total reflection (ATR). NMR spectra of the acetylated lignins (Lundquist 1992) were measured in $CDCl_3$ (c = 100 mg mL^{-1} for ^1H and ^1H / ^{13}C HSQC NMR experiments and c = 200 mg mL^{-1} for quantitative ^{13}C NMR experiments) on a Bruker Avance

DPX300 spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz) using a 5 mm ^{1}H/BB inverse probe with z-gradient support, at 300 K. Chemical shifts were referenced to the residual solvent signals at $\delta(^1H) = 7.26$ ppm and $\delta(^{13}C) = 77$ ppm. Chromium(III)acetylacetonate (0.01 M) was added as relaxation agent for quantitative ^{13}C NMR experiments (Capanema et al. 2004). ^{13}C T_1 relaxation times were monitored with the inversion recovery technique for each sample. To ensure quantitative conditions, inverse-gated ^{1}H decoupled ^{13}C NMR spectra were recorded with 5 s relaxation delay, 0.4 s acquisition time and 245 ppm spectral width. For each spectrum, 65536 transients were accumulated. Quantitative ^{1}H NMR experiments were recorded with 7 s relaxation delay, 4.2 s acquisition time and 26 ppm spectral width. 128 scans were acquired from a sample with no added relaxation reagent. Processing of quantitative 1D spectra involved exponential window multiplication (LB = 0.3 Hz for ^{1}H and LB = 5 Hz for ^{13}C, respectively) of the free induction decay prior to Fourier transform. 2D ^{1}H / ^{13}C HSQC NMR experiments were recorded with 2048 data points in the ^{1}H dimension, 512 time domain increments in the ^{13}C dimension, 256 scans, 0.5 s relaxation delay, 0.21 s acquisition time, and 16 ppm (^{1}H) / 165 ppm (^{13}C) spectral width. 2D time domain data were multiplied with exponential (LB = 3 Hz; ^{1}H dimension) and shifted square sine bell (SSB = 2; ^{13}C dimension) functions and zero-filled to 2048 times 1024 real data points prior to Fourier transform. All 1D and 2D NMR data were processed and analyzed by the Bruker software TopSpin 2.1.

Charcoal

BET surface area was measured on a BELsorp mini II from BEL Inc., Japan according to Brunauer et al. (1938) and IUPAC recommendations (Rouquerol et al. 1994). Pore distributions were plotted in terms of the BHJ- and the MP- plot for meso- and micropores, respectively. The ash content of the ACs was measured according to DIN 38 409 H1-3 (Deutsche-Norm 1987) at a temperature of 850 °C, p*H* in water was measured at a concentration of 50 g L^{-1}.

Pulp analyses

Standard protocols were used for pulp analysis: Kappa number (Tappi 1993), Ox-Dem kappa number (Li and Gellerstedt 2002), HexA content (Gellerstedt and Li 1996), brightness (ISO-2470-1 2009), intrinsic viscosity (SCAN 1988). The degree of polymerization was calculated from the intrinsic viscosity according to Marx-Figini (1978).

4 Autohydrolysis and acid catalyzed hydrolysis

In this chapter, the results published in paper III are briefly summarized. Additional results, which have not yet been published, are also discussed.

Acid prehydrolysis of woody biomass was intensely studied in the last century for a number of purposes - mainly for monosugar and ethanol production. Although the solution and precipitation behavior of lignin caused serious problems in industrial scale and led to the close-down of several plants for environmental reasons (Rabinovich 2009), no thorough investigation on the influence of acid addition on lignin dissolution was performed. Shorter prehydrolysis times and lower temperatures, for example accomplished via acid catalysis, reduce the amount of lignin in the hydrolyzate (Leschinsky et al. 2009). As a consequence also heating costs are reduced, on the other side the utilization of acids causes additional costs. Therefore recirculation possibilities must be kept in mind.

It was therefore the aim of paper III to comparatively evaluate the influence of water autohydrolysis and acid-catalyzed hydrolysis on the dissolution and precipitation behavior of lignin in the hydrolyzates with reference to their potential of providing a substrate for xylan-derived products. Acetic acid, oxalic acid, and the mineral acid sulfuric acid were used as acid catalysts. Acetic acid was chosen for direct comparison to autohydrolysis, because it is the actual catalyst within the autohydrolytic treatment. Current pulping developments aim to avoid the addition of environmentally unfavorable heteroatoms like sulfur or chloride in the pulping system, therefore organic acids offer the possibility of a sulfur free pretreatment that is less corrosive. Therefore the strong dicarboxylic acid oxalic acid was chosen in comparison to sulfuric acid, a conventional hydrolysis catalyst.

4.1 Lignin distribution during acid catalyzed hydrolysis

In order to obtain full information of the lignin mass balance during acid catalyzed hydrolysis, all lignin fractions (Klason lignin and acid soluble lignin of the residual wood, soluble and insoluble lignin in the hydrolyzate) were quantified. Klason lignin (KL) in wood does not decrease with increasing treatment intensity (Figure

12). Acid strength and type of acid do not alter KL content of the hydrolyzed wood at a comparable wood yield level. However, during autohydrolysis a slightly reduced Klason lignin content was observed. It was therefore assumed that KL is not the source of dissolved lignin in the acid hydrolyzates, but might be of some importance during autohydrolysis.

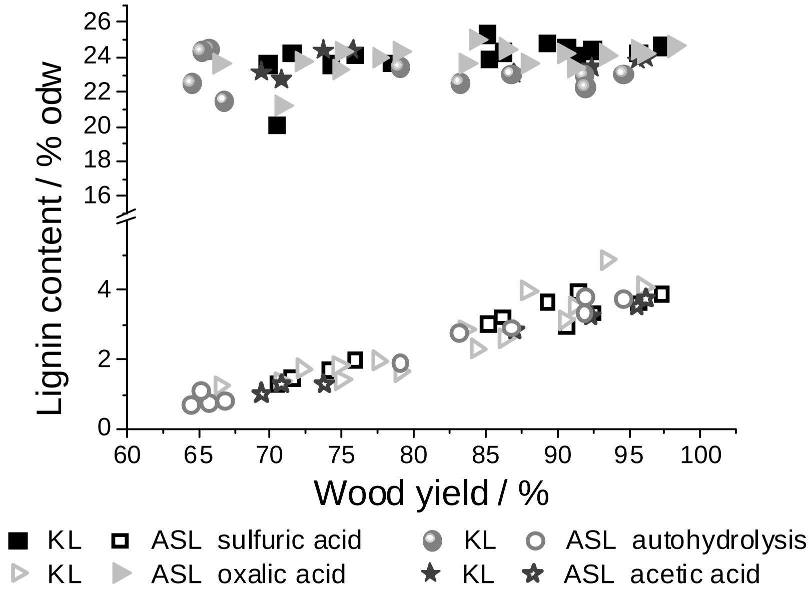

Figure 12: Klason lignin (KL) and acid soluble lignin (ASL) of the wood residues of sulfuric, oxalic and acetic acid pretreatment and autohydrolysis.

With increasing wood loss the amount of acid soluble lignin (ASL) was reduced from 4.8 % odw to below 1 % odw in all experiments to a similar extent. Thus, ASL is the main lignin moiety dissolved in the slightly acidic aqueous hydrolyzates.

In the hydrolyzates two lignin fractions were collected: soluble (S) lignin (Figure 13b) and insoluble (I) precipitated lignin (Figure 13a) that was separated from the soluble fraction via centrifugation. S-lignin in the hydrolyzate increased with decreasing wood yield to the same extent than ASL in the wood residue decreased. The amount of I-lignin did not follow a distinct trend in respect to wood yield, but especially at increased wood yield losses, autohydrolysis and acetic acid hydrolysis showed a considerably higher amount of I-fraction as compared to sulfuric and oxalic acid pretreatments. Thus, ASL was responsible for both I- and S- lignin in sulfuric and oxalic acid hydrolysis, during autohydrolysis the loss in KL adds up to an increased value of I-fraction lignin.

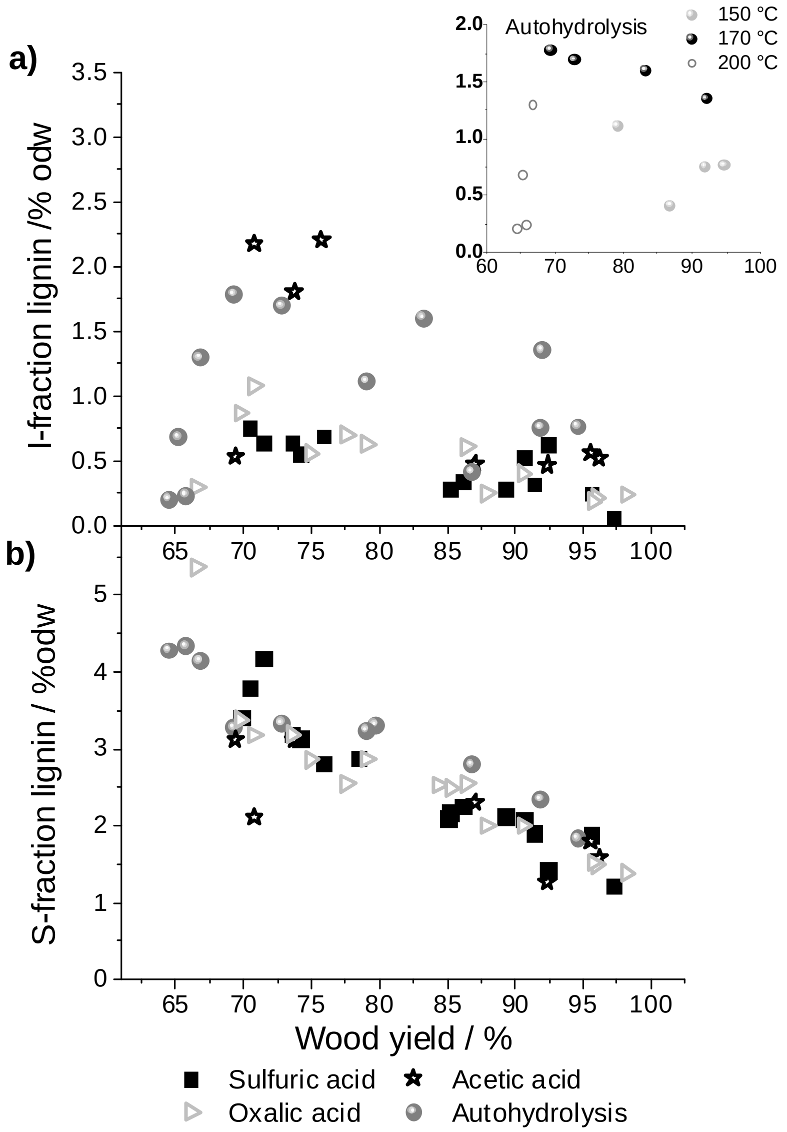

Figure 13: a) Insoluble (I) and b) soluble (S) lignin in the hydrolyzates as a function of wood yield.

The formation of an I-fraction during autohydrolysis is extremely temperature dependent. Experiments performed at 150 °C lead to significantly less I-lignin than experiments performed at 170 °C at similar wood yield levels (Figure 13a). The same trend was visible for acetic acid experiments. The drastic decrease of I-lignin in autohydrolyzates at a process temperature of 200 °C (wood yields of 63 to 68 %) is a consequence of two effects: First, isothermal displacement of the hydrolyzate was not possible at the high water vapor pressure at 200 °C with the existing equipment. Therefore reprecipitation of lignin on the wood chips is assumed, which is supported by an increase in the KL content in the wood residue of two samples (Figure 12). Second, a large fraction of incrustations was formed on the equipment at 200 °C, which was not possible to quantify, but is reported to consist of lignin mainly (Leschinsky, 2009). The immediate formation of incrustations was only monitored for the 200 °C autohydrolysis experiments.

Summarizing the lignin behavior during prehydrolysis, it can be stated that the amount of soluble lignin in the hydrolyzate does not drastically change with the addition of acid. The amount of insoluble lignin however can be decreased by 65 % using oxalic and sulfuric acid catalysts, which should at least facilitate down-stream processing.

4.2 Carbohydrate reactions

The product spectrum apart from lignin is also drastically changed using acid catalysts (see also introduction chapter 2.1). Autohydrolysis liberates xylooligomers, which are only slowly converted to monomers. The subsequent dehydration to furfural occurs to a great extent due to the high temperatures applied. Using acetic acid as catalyst the composition of the hydrolyzates remained basically unchanged in comparison to those resulting from autohydrolysis. Thus, it was concluded that the acidity created by the addition of acetic acid, even in high amounts, is too low to accelerate the hydrolytic cleavage of carbohydrates relative to the pure autohydrolysis process. During oxalic and sulfuric acid catalysis, however, xylooligomers are only liberated at low wood yield levels and are immediately degraded to monomers. Due to the low temperatures applied the formation of furfural is not pronounced. The xylan distribution is exemplified for oxalic acid and autohydrolysis in Figure 14.

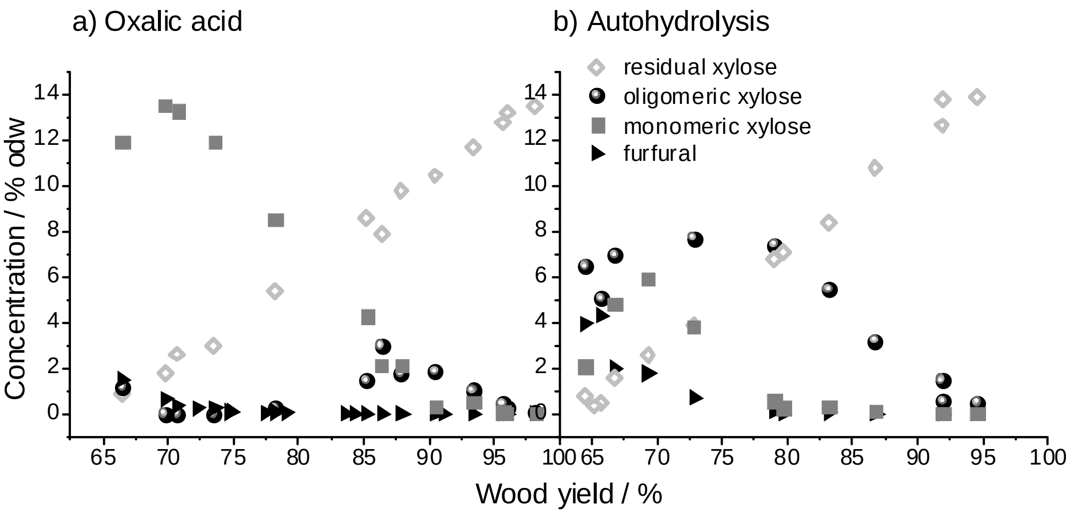

Figure 14: Distribution of xylan during a) oxalic acid and b) autohydrolysis treatment

The oligomeric xylose fraction in autohydrolyzates contains XOS of different degrees of polymerization and charge. Neutral XOS with a DP of 2-6 are monitored in Figure 15. The xylose content decreases from a DP of 1 to a DP of 6, further a high amount of xylose with a DP > 6 and acidic XOS were monitored. Tunc and van Heiningen (2011) reported DPs of 36-71 for xylans precipitated from hardwood autohydrolyzates. It can therefore be concluded that xylose hydrolysis in the hydrolyzate proceeds mostly endwise, as was also reported for XOS derived from hydrothermolysis of xylan isolated from steeping lye, a filtrate from alkalization of pulp for viscose manufacture (Griebl et al. 2006).

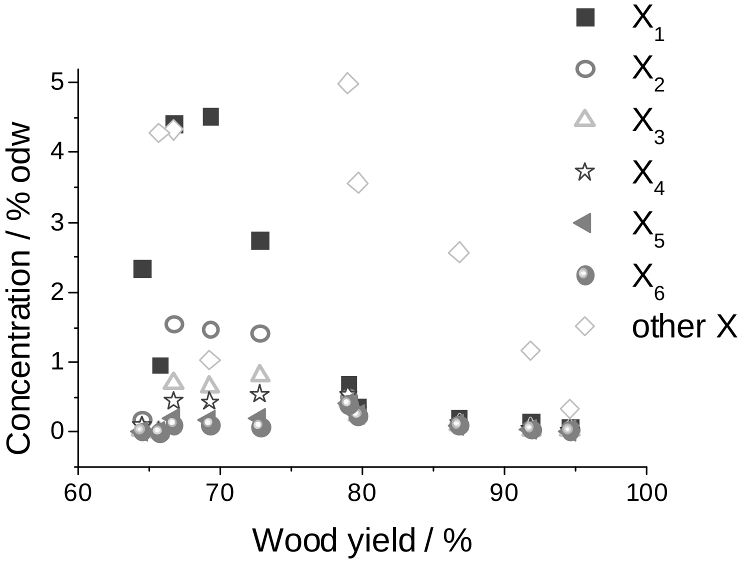

Figure 15: Distribution of monomeric (X_1) and neutral di- to hexameric (X_{2-6}) xylose in autohydrolyzates and other xylose components (other X) including acidic xylooligomers and neutral xylooligomers > X_6 (determined as the difference of total carbohydrates after total hydrolysis and sum of X_1 to X_6)

The amount of glucose in the hydrolyzates is almost negligible up to a wood yield of 80 %. During sulfuric and oxalic acid treatment glucose dissolves more readily with a steeper slope than during autohydrolysis. It is therefore expected, that chain scission within the wood residue also takes place to a higher extent. Thus, pulp yield and viscosity after cooking are expected to be lower using acid catalyzed hydrolysis as compared to autohydrolysis as a pretreatment step.

4.3 Economical considerations

Looking at the economics of the acid catalyzed hydrolysis three mayor points need to be considered: 1) reduced heating energy due to the lower temperatures applied and the shorter treatment times, 2) higher plant capacity due to shorter process cycle times, 3) additional costs of the acid and its recovery. Oxalic acid for example is increasingly consumed during hydrolysis. Oxalic acid losses of up to 80 % were monitored (Figure 16).

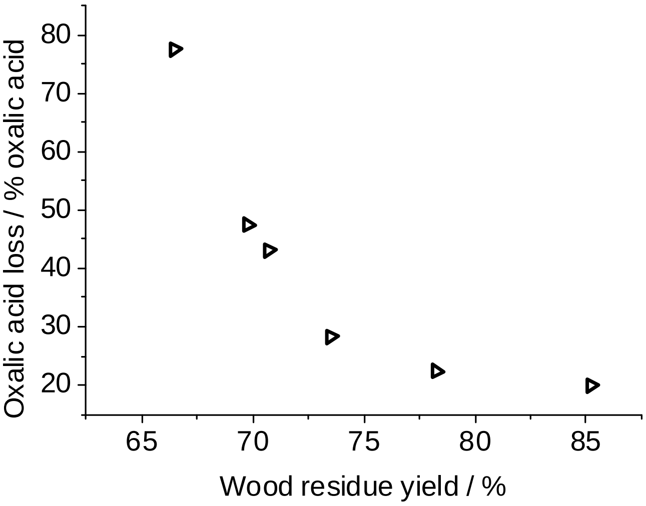

Figure 16: Oxalic acid loss during prehydrolysis.

5 Lignin removal from autohydrolyzates

In chapter 4 it was clearly demonstrated that the dissolution and subsequent precipitation of lignin cannot be avoided. Thus, suitable technologies for the removal of lignin from the process liquors must be developed in order to utilize the carbohydrate fraction.

Within the following chapters two main operational strategies were investigated in order to remove lignin from the hydrolyzates: The influence of adsorbents, primarily activated charcoal, on *Eucalyptus globulus* prehydrolyzates and its colloidally dissolved lignin fraction and the interaction of protein rich sources acting as flocculants with prehydrolyzates. Further on the focus was set on purification methods that are also applicable at high temperatures. Thus, a purification step can be implemented directly after the hydrolysis stage and the formation of lignin incrustations in heat exchanger equipment and the like can be minimized.

5.1 Removal of lignin at room temperature

Physical separation

Centrifugation separates the hydrolyzates into two fractions (Leschinsky 2009): the liquor fraction containing soluble (S) lignin and a solid fraction that consists of insoluble (I) precipitated lignin almost exclusively (Leschinsky et al. 2008a). The S-fraction contained carbohydrates, furfural and still rather high amounts of lignin which accounted for 74 % of the lignin in crude autohydrolyzate. Turbidity of the system could be significantly reduced after centrifugation, but after some hours clouding of the system was observed, indicating ongoing aggregation and precipitation of colloidal lignin fragments.

Filtration of crude autohydrolyzates over a folded filter led to clogging of the filter and filtrates that were still very turbid. Vacuum filtration of the autohydrolyzate over a 0.45 µm filter showed long filtration times and the resulting filtrate had an unaltered high turbidity and lignin content.

Flocculation with protein rich sources

In search of a co-flocculation agent for lignin in hydrolyzates, proteins with good availability like soy, milk or whey proteins where considered as rather suitable.

Polyphenolic compounds like lignin and tannin form complexes with proteins. This effect is also used in fruit juice clarification (Oszmianski and Wojdyło 2007). Proteins show flocculation upon acidic p*H* values. The specific p*H* needed for denaturation thereby depends on their isoelectric point. As protein rich sources soy milk, egg white, whey powder, and various cow milk products (unskimmed, UHT, condensed) were tested. Proteins and lignin formed large flocs that were easily and fast separated from the hydrolyzates by filtration over a Whatman folded filter, unlike crude hydrolyzates that blocked the filter immediately. After filtration the turbidity of the system was significantly reduced by 92 % after addition of 2 % whey powder as compared to autohydrolyzates after centrifugation, equal to 98 % as compared to crude autohydrolyzate. Lignin was reduced by up to 41 % after the addition of protein rich sources and subsequent filtration (Table 5).

Table 5: Maximum lignin removal using protein rich sources.

Protein rich source	Maximum lignin removal / %
Soy milk	39.7
Unskimmed milk	40.7
UHT milk	39.9
Condensed milk	40.2
Egg white	35.5
Whey powder	35.1

Soy milk showed a maximum of lignin removal of roughly 40 % at a concentration of 100 mL L^{-1}. This indicates flocculation due to charge neutralization (Figure 17), additional amounts of protein introduce a charge excess that leads to stabilization of the system that is further promoted by dilution of the system.

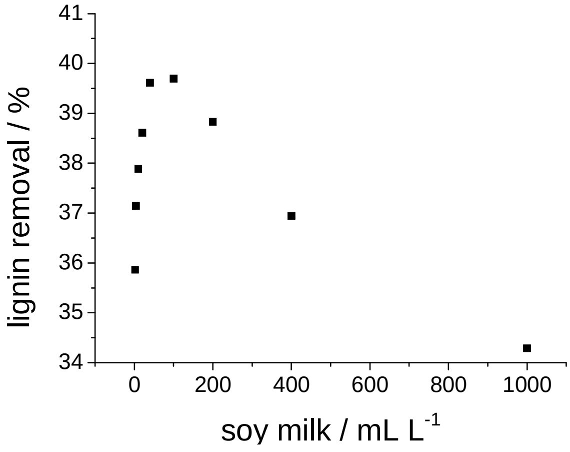

Figure 17: Lignin removal as a function of soy milk addition

Carbohydrates, furfural and HMF were not removed during flocculation and filtration. Furfural would be able to form Schiff bases with the lysine groups of the proteins at the conditions given (Swain et al. 2004), but as denaturation occurs within a short time, phase separation hindered this reaction. Differences between vegetable (soy) and animal (milk, whey) proteins were not noticeable.

Other flocculation agents

Zeta-potential measurements of the autohydrolyzate showed slightly positive zeta-potentials near zero. Therefore it was concluded that ionic additives would not lead to satisfying particle formation. To emphasize this assumption a C_{14}-C_{16} alpha sulfonic acid sodium salt was added as anionic surfactant. As anticipated the addition of this anionic surfactant had no positive effect on the prehydrolyzate. A non-ionogenic surfactant a C_{10} alcohol poly(ethylene oxide) was able to stabilize some part of the lignin, as lignin content after filtration was higher than after centrifugation and filtration times were clearly reduced compared to crude hydrolyzates. Molecular sieves showed no effect at all. Neutralization with $Ca(OH)_2$, as described in literature (Frazer and McCaskey 1989; Griffin and Shu 2004; Han et al. 2006; Kholkin et al. 1999; Khristov et al. 1989; Marton et al. 2006; Parajó et al. 1996a), yielded in faster filtration times, nevertheless lignin concentration in the filtrate was equal to lignin concentration after centrifugation.

Adsorption

Various aluminum oxides, montmorillonites and activated charcoals were tested for lignin removal. The addition of aluminum oxides and subsequent filtration for the separation of aluminum oxide from the hydrolyzates led to a lignin removal similar to that of pure filtration. Montmorillonites increased lignin removal to 35 % which is still far below an acceptable level for efficient hydrolyzate purification.

The utilization of activated charcoals at room temperature, however, allowed a lignin adsorption of up to 95 % depending on the surface area of the charcoal. Concomitant carbohydrate adsorption became pronounced at activated charcoal additions exceeding 10 % odw.

5.2 Removal of lignin at prehydrolysis temperature - The HiTAC-process

In this chapter, the results published in the patent application VI and the papers I and II are briefly summarized and discussed.

The objective of the following chapters was to develop a process for the removal of lignin and lignin degradation products from the autohydrolysis liquor immediately after its discharge from the hot pressurized reactor in order to prevent excessive precipitation. Activated charcoal proved to be efficient and selective for lignin removal at room temperature. Furthermore, charcoals show a sufficient thermal stability to be tested for high temperature applications. The efficiency and selectivity of this HiTAC process (high temperature adsorption on activated charcoal) should be investigated in detail. Within a temperature range of 20 °C to 170 °C, the effects of adsorption temperature, adsorption time and the type and amount of activated charcoal were examined.

5.2.1 Adsorption of hydrolyzate components

The adsorption of lignin on activated charcoal at room temperatures gave promising results in respect of lignin adsorption capacity and selectivity towards lignin. In order to evaluate the potential of lignin adsorption directly after its discharge from the prehydrolysis reactor at high temperatures a second heated reactor containing activated charcoal mixed with water was connected to the prehydrolysis reactor (Figure 18).

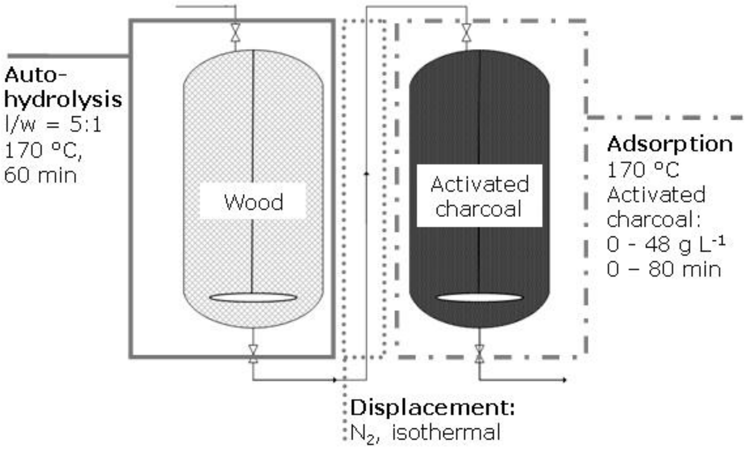

Figure 18: HiTAC reactor system.

The addition of activated charcoal (AC) at prehydrolysis temperature, even in amounts far lower than those recommended in the literature (Parajó et al. 1996b), could prevent the formation of incrustations in the second reactor efficiently. Adsorption time had only a minor effect on lignin adsorption at 170 °C and almost complete adsorption was accomplished within less than 10 min. As sugar decomposition at 170 °C started to be significant when exceeding 20 min of treatment time and handling was easier and more reproducible using longer times, the adsorption time was set to 20 min for further experiments.

With increasing charcoal concentration lignin was continuously removed from the hydrolyzate up to a lignin removal of 96 % at the highest charcoal concentration applied (Table 6). At charcoal concentrations below 24 g L^{-1}, corresponding to a lignin removal of 85 %, carbohydrate adsorption is negligible. At higher charcoal concentrations oligomeric xylan is increasingly adsorbed, monomeric sugars remain unaffected. Parallel to lignin adsorption, furfural and HMF are removed from the hydrolyzate. Lignin, furfural, and HMF are inhibitors for most enzymes used for carbohydrate conversion to valuable products. The amounts of lignin, furfural and HMF in *Eucalyptus globulus* water prehydrolyzates, subjected to the HiTAC process, are at a sufficiently low level for fermentation processes (Cruz et al. 1999; Keller and Nguyen 2001; Mendes et al. 2009; Parajó et al. 1998; Villarreal et al. 2006).

Table 6: Composition of prehydrolyzates after 20 min adsorption onto AC (BET 880 m^2 g^{-1}) at 170°C

	Concentration of the compounds (mg L^{-1}) after treatment with AC concentrations (g L^{-1})						
Compounds	0	8	12	20	24	32	48
Lignin	9680	5634	4391	2972	1559	921	376
Sugar total[1]	23368	23711	23631	23398	22184	20732	18983
Sugar oligo[2]	13119	12680	13108	13661	11574	10481	6941
Xylose oligo[2]	11212	10810	11218	11609	9678	8965	5236
Xylose mono[3]	7664	8231	7796	7190	7918	7595	9348
Glucose oligo[2]	515	588	579	585	572	436	406
Glucose mono[3]	293	326	324	274	335	293	434
Galactose oligo[2]	525	544	581	614	512	467	437
Galactose mono[3]	1191	1283	1275	1205	1252	1242	1342
Furfural	1555	1477	1167	1068	720	333	237
HMF	172	153	127	137	118	71	49
Acetic acid	3083	3341	3531	3557	3496	3182	4175
Incrustation[4]	430	-	-	-	-	-	-

[1] after total hydrolysis, [2] oligomeric fraction: difference in sugar content before and after total hydrolysis, [3] before total hydrolysis, [4] incrustations from the reactor equipment dissolved in NaOH

5.2.2 Adsorption isotherms

The adsorption of lignin can be conveniently fitted by the Freundlich adsorption model (Figure 19). The Freundlich adsorption isotherm describes adsorption in a monomolecular layer and additionally relates the concentration of the solute on the surface of the adsorbent, to the concentration of the solute in the liquid phase in a logarithmical relationship. Freundlich equation can be written as:

$$q_e = k_f \cdot C_e^{1/n} \qquad (2)$$

where q_e is the amount of lignin adsorbed per unit mass of activated carbon (mg g^{-1}), C_e is the equilibrium concentration of lignin in solution (mg L^{-1}), k_f is the Freundlich constant related to the adsorption capacity (mg g^{-1} (mg $L^{-1})^n$), and n is a dimensionless empirical parameter representing the heterogeneity of the surface.

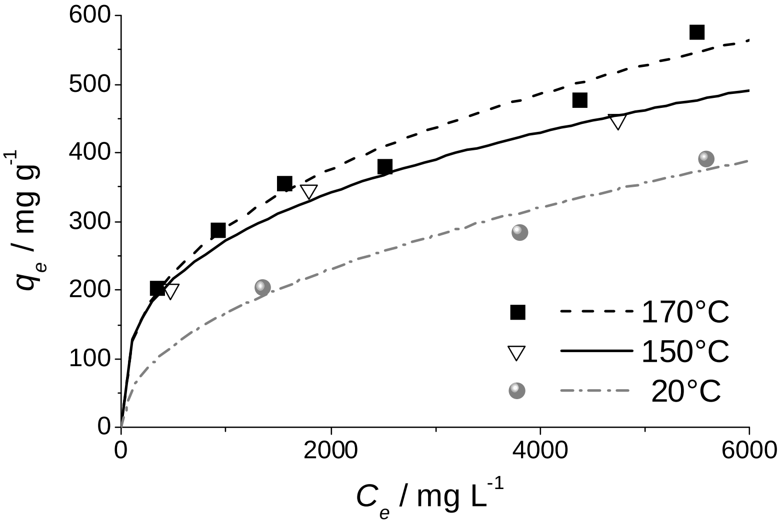

Figure 19: Freundlich isotherms (curves) and experimental adsorption data (individual points) of lignin on activated charcoal (BET surface area 880 m^2 g^{-1}) at different temperatures (20, 150 and 170 °C). q_e amount of lignin adsorbed per unit mass of AC, C_e equilibrium concentration of lignin in solution).

At elevated temperatures the amount of lignin adsorbed per unit mass of adsorbent (q_e) significantly increased, indicating more efficient adsorption. Therefore it was suggested that the lignin in solution at 170 °C exhibits a different structure than at room temperature or even is in liquid state. The arrangement of hydrophilic and hydrophobic groups in this state might favor the adsorption onto activated charcoal. Furthermore, it was proposed that the adsorption of lignin on AC at high temperatures follows a chemisorption process as indicated in the literature (Venkata Mohan and Karthikeyan 1997) and in the desorption experiments with limited success (see chapter 7.1). Elevated temperatures might provide the activation energy required for a chemisorptive process. We further suspect a change in the adsorption mechanism at temperatures beyond 100 °C, as Parajó found that in the range between 20 and 60 °C the adsorption efficiency decreased significantly with increasing temperature (Parajó et al. 1996a)

Lignin adsorption capacity of the charcoals increased with increasing BET surface area (Figure 20), but not linearly. The total surface area (calculated as the product of BET-area and amount of charcoal) needed for a similar lignin removal was 70 % higher for the charcoal of BET 880 than of BET 1270 $m^2\ g^{-1}$. This discrepancy can be explained by different pore size distributions. All charcoals investigated showed small micropore and mesopore diameters. The volume of mesopores and the micropore diameter was significantly higher for the charcoal with the best performance (BET 1270 $m^2\ g^{-1}$). The charcoal with the worst performance (BET 280 $m^2\ g^{-1}$) had in total very low volumes of both meso- and micropores. Potential effects of the ash content and the alkalinity of the ACs on the lignin adsorption are possibly superimposed by the high differences in BET surface area and pore distribution. The alkalinity of the AC might affect the stability of carbohydrates during the adsorption process.

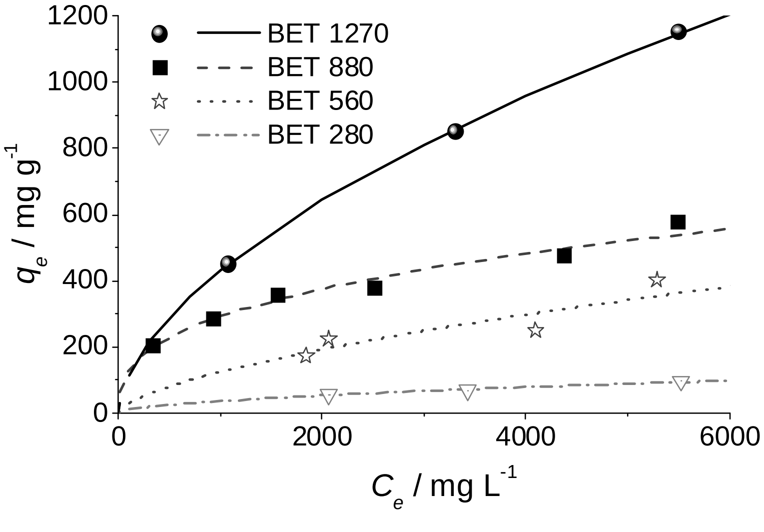

Figure 20: Freundlich isotherms (curves) and experimental adsorption data (individual points) of lignin on activated charcoals of BET surface areas of 1270, 880, 560, 260 $m^2\ g^{-1}$ for 20 min at 170°C. q_e amount of lignin adsorbed per unit mass of AC, C_e equilibrium concentration of lignin in solution.

During HiTAC-processing the surface area of the charcoals is drastically decreased, e.g. from 880 to 70 $m^2\ g^{-1}$ (at a charcoal dosage of 20 g L^{-1} and 20 min adsorption time.), which is considerably lower than known for other applications (Chestnutt et al. 2007). Electron microscopy images show the structured surface of the activated charcoal. After the adsorption process a smooth surface covered with lignin is imaged (Figure 21). The low surface area of spent charcoals from the HiTAC-process probably originates from polymerization of the lignin on the surface at the high temperatures applied during the adsorption step (Dabrowski et al. 2005; Leschinsky et al. 2008a). The low surface area of the spent charcoal will be disadvantageous for charcoal recycling (see chapter 7).

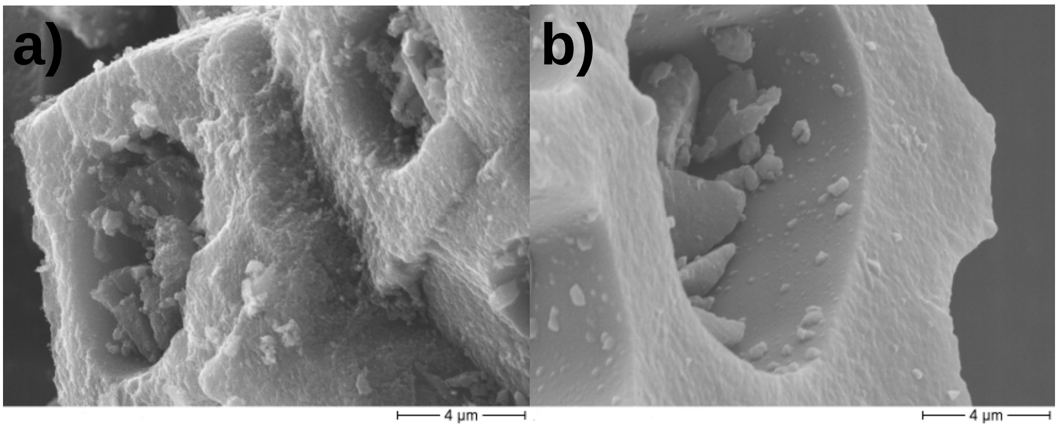

Figure 21: SEM images of activated charcoal a) before and b) after lignin adsorption.

6 Characterization of xylans from HiTAC-treated hydrolyzates

The HiTAC-process described in Chapter 5.2 provides purified autohydrolyzates containing monomeric and oligomeric xylose mainly. In the following xylooligomers were precipitated and analyzed to provide a data basis for potential applications. Core results of this chapter were also presented in publication number 5.

6.1 Yield of the precipitated xylan fraction

Ethanol addition to aqueous autohydrolyzates is expected to precipitate the higher molecular weight XOS fraction. The lower the prehydrolysis intensity, the less degradation of XOS takes place and the more XOS can be precipitated via ethanol precipitation (Figure 22). It needs, however, to be noted that the overall xylan solubilization at short prehydrolysis times is low. Thus, the highest yield of precipitated XOS (2.4 % odw) was observed for P-factor 250 experiments at 150 °C where also the total xylan solubilization is considerably high (8 % odw), but xylan degradation is still low. Ethanol precipitation of autohydrolyzates produced at 200 °C yielded low amounts of precipitate, which was a calcium salt mainly.

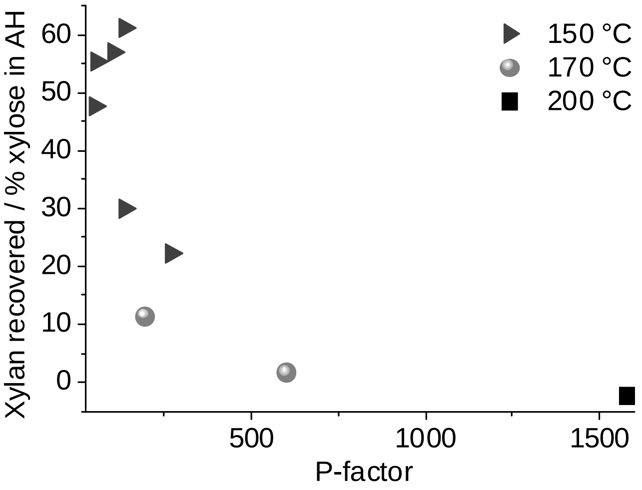

Figure 22: Recovery of xylans via ethanol precipitation

6.2 Chemical composition of precipitated xylan fraction

The main component of the ethanol precipitated fraction of autohydrolyzates produced at 150 and 170 °C was highly substituted xylan (Table 7). Additionally, substantial amounts of glucose were precipitated at a xylose to glucose ratio that approximately correlates to the oligomeric xylose to oligomeric glucose ratio in the hydrolyzates. The degree of substitution of the xylan precipitated from hydrolyzates produced at 170 °C is well in agreement with the data reported by Leschinsky (2009) for the total soluble hydrolyzate. Thus, it is assumed that the substitution pattern of the precipitated xylan fraction is representative for the total carbohydrates in the hydrolyzate. Xylan precipitated from hydrolyzates produced at 150 °C showed a substantially higher degree of acetylation than from 170 °C hydrolyzates. It seems that, although similar P-factors were performed, deacetylation is slower at 150 °C than at higher temperatures. With increasing reaction time a decrease in acetyl groups was observed at 150 °C which is in agreement with the results obtained by Testova et. al. (2011) for birch autohydrolyzates.

Table 7: Chemical composition of the ethanol precipitated hydrolyzate fraction

P-temp / °C	170	150	150
P-time / min	20	68	129
P-factor / h	193	136	258
Xylan yield recovered / % odw	0.6	1.0	2.4
Xylan yield recovered / % oligo. xylan	12.2	30.9	31.9
Composition anhydrosugars / %ods			
Xylose	36.3	39.8	55.8
Glucose	8.4	7.9	5.6
Rhamnose	1.3	2.3	1.9
Arabinose	0.1	0.3	0.1
Galactose	6.1	7.2	6.7
Mannose	4.7	3.9	3.3
Composition substituents / %ods			
Galacturonic acid	1.7	5.5	3.2
DS Galacturonic acid	*0.04*	*0.10*	*0.04*
4-O-Methyl-glucuronic acid	5.6	8.7	11.5
DS 4-O-Methyl-glucuronic acid	*0.11*	*0.15*	*0.14*
Glucuronic acid	0.5	0.7	0.7
DS Glucuronic acid	*0.01*	*0.01*	*0.01*
Acetyl	2.3	9.1	10.7
DS Acetyl	*0.15*	*0.51*	*0.47*
Sum / %ods	67.0	85.4	99.5

DS degree of substitution; % ods oven dry substance

In contrast, Leschinsky et al. (2009) reported a rather constant degree of acetylation with proceeding hydrolysis of *Eucalyptus globulus* at 170 °C, the same was observed by Tunc and Van Heiningen (2008) for southern hardwoods at 150 °C. Garrote et al. (2001), however, found a decreasing degree of acetylation of XOS in *Eucalyptus globulus* autohydrolyzates with increasing reaction time. The degree of *4-O*-methyl-glucuronic acid substitution of the precipitated xylan was again higher at 150 °C than at 170 °C. The high degree of total substitution and the possibility to tailor the substitution pattern by temperature variations might be interesting in regard to product characteristics and application areas of the XOS fraction.

6.3 Molecular weight distribution of the precipitated xylan fraction

Although a washing step was applied after xylan precipitation, all xylans show a bimodal molar mass distribution where the low molar mass peak is in the area of monomeric xylose. Xylan precipitated from 150 °C autohydrolyzates consists mainly of high molecular mass components, with increasing treatment time the high molecular mass peak is, however, shifted to lower molar masses due to the degradation of the xylan (Figure 23a).

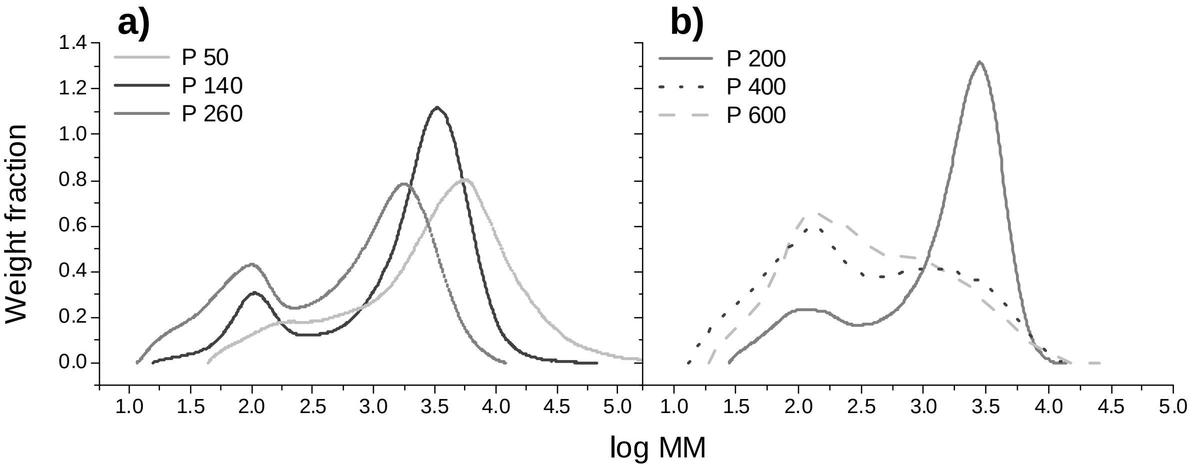

Figure 23: Molecular weight distribution of xylan precipitated from autohydrolyzates produced at a) 150 °C and b) 170 °C at three different P-factors.

At 170 °C the same shift of the high molar mass peak towards lower molar masses was observed with increasing treatment time, parallel the ratio of low molar masses to high molar masses changed in favor of the monomeric components (Figure 23b) which is in agreement with the results obtained from the total hydrolyzates where ongoing degradation of XOS to monomeric xylose and furfural was observed (paper III). Although xylans that were prepared from autohydrolysis experiments at different temperatures but at similar P-factors showed a different substitution pattern, the molecular weight distributions of these xylans are rather similar (Figure 24). Thus, the hydrolysis of the xylan backbone is sufficiently described by the P-factor model, while the hydrolysis of side groups depends on the applied temperature.

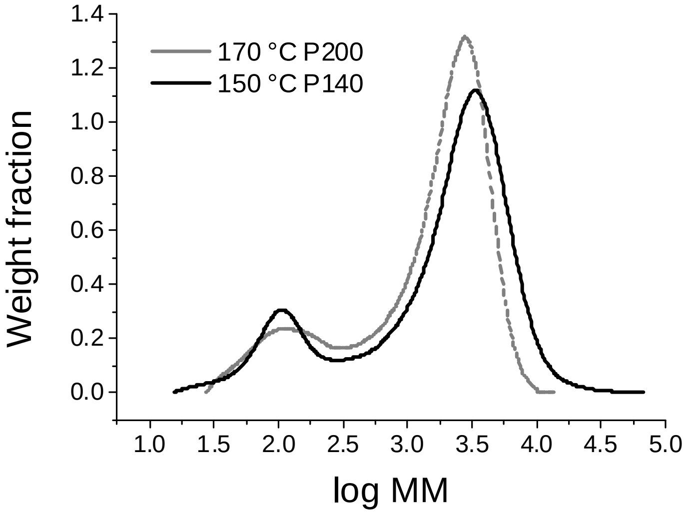

Figure 24: Molecular weight distribution of xylans precipitated from autohydrolyzates produced at 150 and 170 °C at a similar P-factor level

7 Regeneration of spent charcoals

The last two chapters showed the high potential of HiTAC-processing for the production of xylan derived products from autohydrolyzates. The implementation of this technology in industry, however, is indispensably linked to the solution of one major economical and/or technological challenge: an appropriate technology for the regeneration of the spent charcoal and its reutilization in the process is needed, as activated charcoal is a high cost factor in the amounts needed for a pulp mill.

The following section is based on paper IV and aims at the development of adequate recycling and regeneration strategies for spent activated charcoals from the HiTAC-processing of *Eucalyptus globulus* autohydrolyzates. Solvent extraction and thermal regeneration of spent charcoals were applied in order to regain a charcoal of high surface area and microporosity that can be recycled in the HiTAC-process.

7.1 Solvent desorption

It is indicated in literature, that the inductive effect of methoxyl- and ethoxyl substituents of phenols leads to a strong binding to the charcoal matrix and to a high degree of irreversible adsorption. High temperatures are said to further enhance chemisorption and to lead to polymerization reactions on the charcoal (Dabrowski et al. 2005). These effects are likely to occur when autohydrolysis lignin is adsorbed at high temperatures, because autohydrolysis lignin shows a high degree of methoxyl-groups (20 %) (Leschinsky et al. 2008a). To validate this assumption desorption tests using various lignin solvents were performed. Up to 21 % of the lignin on the charcoal could be removed using DMSO as solvent (Table 8). Still, the BET surface area was far below an appropriate range for efficient further lignin adsorption.

It can be assumed that lignin solvents other than the ones tested, e.g. ethylacetate and ionic liquids, are not capable to fully dissolve the lignin in the charcoal pores either. Repeated utilization of the solvent extracted charcoals showed adsorption of lignin that could not only be attributed to adsorption on the available surface area. It was therefore assumed that polymerization reactions of lignin on the lignin covered surface occur. Thus, chemisorptive mechanisms explain the low solubility of lignin from the coal after the HiTAC-process, which in turn means that solvent extraction is not a viable recycling technology to restore the adsorption capacity of activated carbons following a HiTAC-treatment of autohydrolyzates.

Table 8: BET surface after solvent desorption of lignin.

Solvent	Dissolved lignin (% lignin on AC)	BET ($m^2 g^{-1}$)
Water	-	70
NaOH (0.5 N)	10	109
Acetone/water (5/1)	21	122
Ethanol	10	95
Acetic acid	18	106
DMSO	n.d.	134

7.2 Thermal reactivation

Thermal reactivation (TR) of spent activated charcoals is performed when other recycling strategies fail. This process will contribute to the profitability of the adsorption process and to the eco-friendliness, as the carbon is reactivated in lieu of landfilling and incineration, provided that the original surface area and pore size distribution is recreated. A thermal reactivation process at 950 °C for 30 min under CO_2 atmosphere met these requirements (Figure 25) and maintained a yield of 96 %.

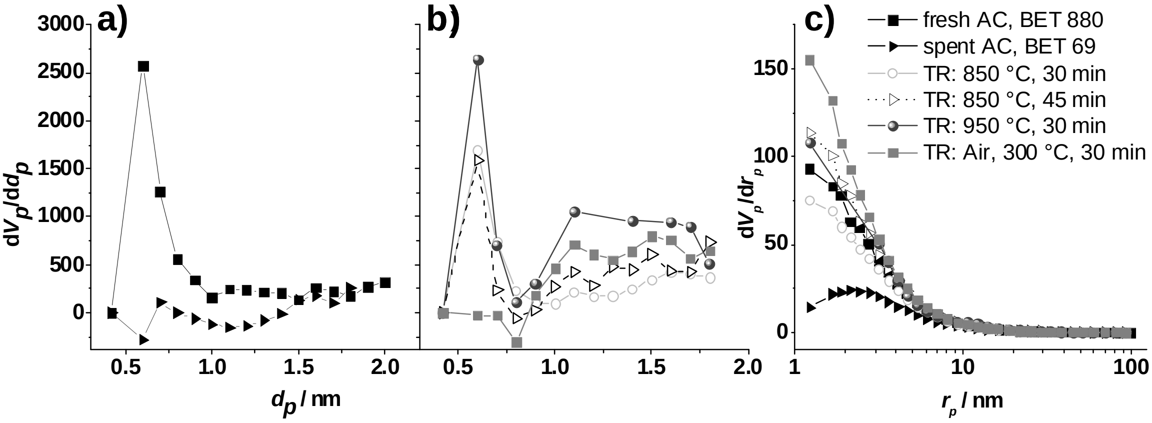

Figure 25: Micropore distribution of a) virgin and spent AC and b) thermally regenerated charcoals c) mesopore distribution of all charcoals.

The original charcoal showed a high fraction of small sized micropores (d_p < 1 nm) and small mesopores (r_p 1-10 nm), while the spent activated charcoal after the HiTAC-process was lacking small micropores and contained less and smaller mesopores. Obviously, those sites were preferably occupied by firmly attached lignin moieties as indicated by the high resistance towards solvent desorption (see chapter 7.1). Thermal treatment at 850 °C for 30 min increased the specific surface area of the activated carbon to 605 $m^2 g^{-1}$ and further to 641 $m^2 g^{-1}$ when prolonging the reaction time to 45 minutes. Pore size distributions of these charcoals was similar to the original charcoal, but exhibited a lower volume of small micropores. The yield of the recycled activated carbons was 106 and 108 %, respectively, obviously owing to the partial conversion of the adsorbed lignin into activated carbon. A higher reactivation temperature of 950 °C led to a surface area close to that of the fresh carbon (830 $m^2 g^{-1}$ vs. 880 $m^2 g^{-1}$) and to an almost identical pore size distribution. Subjecting a fresh sample of activated carbon to the same treatment conditions (950 °C, 30 min) resulted in a yield of only 83 %. However, this mass loss was clearly compensated by a drastic increase of the BET surface area to 1075 $m^2 g^{-1}$ (+ 22%), resulting from an increase in both micropore and mesopore volumes (Figure 26).

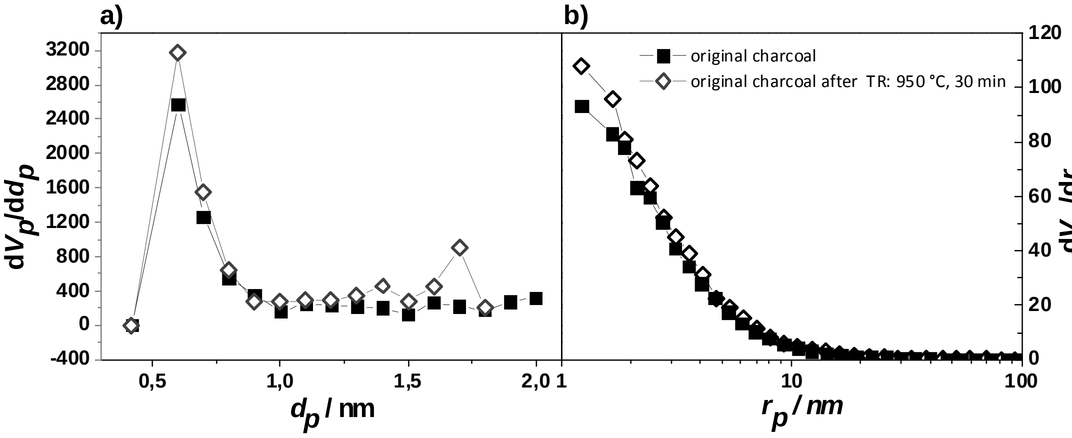

Figure 26: a) Micropore distribution and b) mesopore distribution of original charcoal and after thermal regeneration of original charcoal

These results allow two possible explanations: 1) the lignin on the spent AC is not simply removed from the coal, but transformed to charcoal of a considerably high surface area; 2) the lignin attached to the spent AC protects the AC from thermal degradation, but is itself totally removed within the thermal reactivation step. Due to the fact that lignin is used as a raw material for charcoal production (Zou and Han 2001), it is, however, assumed that the former explanation represents reality more closely.

Application tests of the thermally reactivated charcoals showed that the specific lignin adsorption capacity can be described sufficiently well by the specific surface area of the charcoals (Figure 27). An effect of pore size distribution on lignin adsorption, however, was not observed. Generally, the charcoals regenerated at 850 and 950 °C showed a high selectivity towards lignin, nevertheless up to 10 % xylooligomers and up to 8 % monomeric xylose were adsorbed using both fresh and thermally regenerated charcoals.

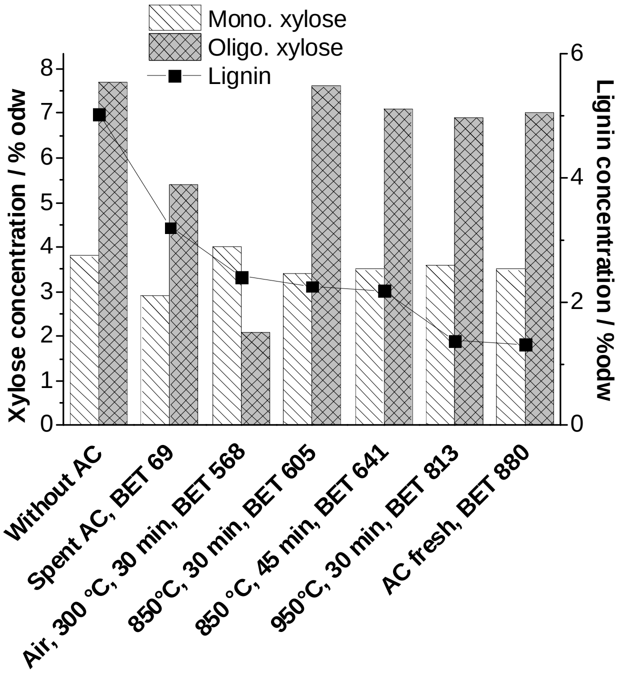

Figure 27: Lignin and carbohydrates in the HiTAC-treated hydrolyzates using thermally reactivated charcoals at a concentration of 20 g L^{-1}.

In order to reduce energy costs during recycling the regeneration in oxygen containing atmosphere at 300 °C was tested as an alternative to high temperature reactivation. The resulting charcoal exhibited a rather low total surface area (568 m^2 g^{-1}). The charcoal showed a completely different pore size distribution as compared to the charcoals regenerated in CO_2-atmosphere: the amount of small mesopores (r_p 1-10 nm) and large micropores (d_p 1-1.7 nm) was distinctly increased, but the high number of small micropores (d_p < 1 nm) was not restored. Thus the micropore structure resembled that of spent AC. Obviously, the combination of oxygen-containing atmosphere and low temperatures was not able to convert the polymerized lignin moieties to a microporous charcoal. Instead it widened the mesoporous structure, which is known to favor hemicellulose adsorption (Montané et al. 2006). When reutilized in the HiTAC-process, this charcoal showed a lignin adsorption proportional to its BET surface area, but also severe adsorption of oligomeric xylose (72 %). Further, the treatment in oxygen-containing atmosphere possibly initiated the formation of carboxylic surface groups that might favor the adsorption of carbohydrates (Duràn-Valle et al. 2005).

8 Residual lignin in pulp

The following discussion is based on paper V.

During prehydrolysis-kraft and soda-anthraquinone cooking macromolecular lignin undergoes a series of degradation and condensation reactions. The unfavorable acid catalyzed reactions during prehydrolysis lead to the dissolution of lignin and further on to the formation of incrustations (Chapter 2.1 and 4) (Leschinsky 2009). During the cooking step lignin decomposition and dissolution are the target reactions and the bulk of lignin is removed from the wood matrix. For a comprehensive understanding of the reactions occurring during pulping it is important to isolate and characterize a representative lignin fraction from the pulp. Various isolation methods are suited for this purpose: milled wood lignin (MWL) (Björkman 1956) dissolved wood lignin (DWL) (Fasching et al. 2008), acidolysis (Evtuguin et al. 2001; Gellerstedt et al. 1994), enzymatic hydrolysis (EH) (Chang 1992; Yamasaki et al. 1981) and the combined method of enzymatic mild acidolysis (EMAL) (Argyropoulos et al. 2000). In this thesis acidolysis was chosen for lignin isolation as it is a simple and rapid method and the resulting acidolysis lignin (AL) is of high purity.

AL contains less etherified units and more free phenolic functions in comparison to native lignin and to enzymatically isolated lignin from *Eucalyptus globulus* kraft pulps (Duarte et al. 2000; Pinto et al. 2002). *β*-*O*-4 bonds split, thus molar mass of the lignins is reduced (Al-Dajani and Gellerstedt 2002; Jääskeläinen et al. 2003). AL contains unsaturated structures and non-lignin materials of polysaccharide origin and condensed tannins of catechin and gallocatechin types, which are said to be removed by an alkaline extraction (AE) prior to acidolysis of wood (Evtuguin et al. 2001). This approach was also applied for kraft pulps (Rutkowska et al. 2009) as at the end of pulp washing, lignin reprecipitates on the pulp due to the reduced alkalinity at the end of the cook. The positive effect of an alkaline extraction stage on the purity and representativeness of isolated lignin from pulp, however, was not yet clarified.

8.1 Influence of pretreatments for lignin isolation on the residual lignin in pulp

Acidolysis according to the protocol of Evtuguin et al. (2001) includes extraction stages with acetone and alkali before the acidolysis step itself is applied. Acetone extraction (AcE) led to a slight decrease of the kappa number from 14 to 13.5. Subsequent AE yielded in a clear kappa number reduction of 2 units (Table 9). Regardless of whether AE was applied or not, kappa numbers of the pulps after acidolysis dropped to an average value of 2.5. Not only lignin contributes to the Kappa number, but also aliphatic double bonds, free aldehyde groups as well as *α*-keto-carboxylic acids (Li and Gellerstedt 2002). The Ox-Dem kappa number represents the kappa number attributed to lignin only (Li and Gellerstedt 1997).

Table 9: Kappa, Ox-Dem kappa, and HexA contents at different extraction stages. AcE: acetone extraction. AE: alkaline extraction.

	Pulp preparation				
	Soda-AQ pulp	AcE	AE	Acidolysis	
				with AE	without AE
Total kappa	14.0	13.5	11.5	2.6	2.4
Ox-Dem kappa*	7.4	6.5	6.0	0.8	1.4
HexA** (≈ kappa)***	27.2 (2.3)	27.9 (2.4)	29.3 (2.5)	---	---

* kappa attributed to lignin (Fasching et al. 2008; Ralph et al. 2004; Robert 1992)

** HexA given in µmol g^{-1} o.d. pulp

*** kappa attributed to HexA (Sixta 2006)

Ox-Dem kappa dropped one unit during AcE and 0.5 points during AE, indicating a higher selectivity of AE. Within acidolysis of the pulps, similar amounts of lignin were removed from pulps with and without AE as revealed by equivalent Ox-Dem kappa reductions (Δ Ox-Dem kappa 5.2 with AE and 5.1 without AE). During acidolysis, the drop in kappa number was higher than the drop in Ox-Dem kappa. Thus, substantial amounts of substances, which did not contribute to Ox-Dem kappa, were removed in addition to lignin within the step of acidolysis.

8.2 Characterization of residual lignin

Although similar amounts of lignin were removed from both pulps within acidolysis, the lignins showed different precipitation behavior in water in the recovery procedure. Lignin from alkaline extracted pulp precipitated only in minor amounts.

Table 10: Characterization of the isolated lignins with AE and without AE.

Lignin	Sugar (%)	Elemental analysis (%)					OMe (%)	C_{900} formula*	Lignin yield (mg g^{-1})
		C	H	N	O	S			
with AE	< 1	60.4	5.9	0.2	33.3	0.2	17.3	$C_{900}H_{852}O_{306}(OCH_3)_{112}$	4.62
without AE	1.2	58.4	5.7	0.2	29.7	0.2	17.6	$C_{900}H_{833}O_{270}(OCH_3)_{118}$	6.68

* values are corrected for sugar impurities

Structural analyses of both lignins with prior AE and without prior AE showed high similarities in lignin structure (Table 10 and Table 11). Both isolation procedures yielded rather pure lignins with very low sugar content (about 1%). The C_{900} formula, calculated from methoxy group content and elemental analysis, showed slightly higher oxygen and hydrogen contents for lignin with AE than for lignin without AE (Table 10). Structural analysis via HSQC and quantitative ^{13}C NMR experiments did not reveal any further differences between the isolated lignin fractions (Table 11). Thus, AE resulted in significant lignin yield losses of 31 % (Table 10), but despite the extraction of non lignin components it does not lead to a lignin of higher purity.

Table 11: Chemical shifts of resonances for integration of peaks in quantitative ^{13}C NMR spectra.

Functional group	Chemical shift (ppm)		*Lignin*	
	from	to	with AE	without AE
prim. aliph. OH	171.0	169.8	0.67	0.64
sec. aliph. OH	169.8	168.8	0.29	0.29
phenol. OH	168.8	167.5	0.42	0.49
O-subst. arom. C**	162.0	142.0	2.26	2.25
C-subst. arom. C***	142.0	125.0	1.82	1.84
H-subst. arom. C	125.0	101.5	1.91	1.91
β-β /α	86.0	85.2	0.04	0.02
β-O-4/β	81.0	79.8	0.13	0.13
methoxy group	57.0	54.5	1.22	1.35

* ^{13}C integral area of the acetylated sample per aromatic unit normalized to the integral area corresponding to methoxy groups

** non-etherified phenolic C-O-Ac added to integral area

*** non-etherified phenolic C-O-Ac deduced from integral area

9 Conclusions and outlook

This thesis provides a purification strategy for prehydrolysis liquors from prehydrolysis-kraft pulp mills, enabling the recovery of valuable hemicelluloses.

It was found that the acid catalysis of the autohydrolysis reaction does not prevent lignin dissolution to an extent necessary for uninhibited hemicellulose recovery. Instead, the product spectrum is shifted from xylooligomers to monomers (in the case of hardwoods and annual plants). In case the formation of monomers is the target reaction (for example for further bioethanol or furfural production), still, the accelerated hydrolysis of cellulose and its effect on subsequent kraft pulping must be kept in mind.

High temperature adsorption of lignin on activated charcoals, a process we named HiTAC-process, led to lignin removal rates of up to 75 % without concomitant adsorption of carbohydrates. At the expense of oligomeric carbohydrate losses, lignin adsorption capacities of 100 % were possible. Generally, the utilization of activated carbons with a high overall surface area, a high number of small micropores and only few mesopores is recommended for ensuring both, high adsorption selectivity and capacity.

The thermal reactivation of the spent charcoals at temperatures exceeding 850 °C under CO_2-atmosphere presumably led to the transformation of the adsorbed lignin to activated charcoal. Thermal reactivation at 950 °C for 30 min showed the best results and a pore size distribution and adsorption characteristic similar to fresh charcoal. Still, there is space for operational optimization. The thermally reactivated charcoal was successfully recycled in the HiTAC-process. Yet, it needs to be checked how many recycling cycles are possible without capacity and selectivity losses.

Future work needs to concentrate on the scale-up of the laboratory results to pilot plant size and on the implementation of these unit operation steps in an industrial integrated process cycle. The use of adsorber beds for lignin adsorption might introduce further problems, because the inlet of the adsorber bed is rather likely to plug due to the high tendency of hydrolyzates to form incrustations. After prehydrolysis in the digesters, the prehydrolyzates can be introduced into a stirred adsorption tank with a short retention time (e.g. 10 min) as only very short adsorption times are necessary for complete adsorption. A thorough distribution of the activated charcoal will be necessary in order to prevent scaling at dead zones of the vessel. A core step will be the separation of the activated charcoal from the hydrolysis liquor, which was conducted in form of dead end filtration using a 0.45 µm membrane in laboratory. This is also a plausible option in industrial scale. Therefore the adsorption step can be followed by parallel filter units (for example press filters or cartridge filters) which can be deloaded alternately. Further options for the separation of the charcoal from the carbohydrate containing hydrolyzate include sedimentation of the charcoal or centrifugation. Weather this separation step should be conducted before or after cooling deserves further optimization. All these unit operation steps are highly dependent on weather a powdered or granular charcoal is used. Granular charcoal is more easily separated, but the adsorption efficiency of granular types was not yet tested.

The wet spent charcoal can be further processed with screw pumps to a regeneration hearth. After thermal reactivation and the addition of make-up coal the reactivated charcoal can be reused in the adsorption step.

Furthermore the subsequent processing of the hydrolyzates for the separation of oligomeric and monomeric carbohydrates needs to be clarified in order to get a well-defined basis for marketable products.

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11 Appendix

List of abbreviations

%odw	Per cent oven dry wood
%odp	Per cent oven dry pulp
%ods	Per cent oven dry substance
AC	Activated charcoal
AH	Autohydrolyzate, autohydrolysis
ASL	Acid soluble lignin in wood and wood residues
CBC	Continuous batch cooking
DP	Degree of polymerization
DS	Degree of substitution
F	Furfural
FTIR	Fourier-transform infrared spectroscopy
GOS	Glucooligosaccharides
HAc	Acetic Acid
HPAEC	High performance anion exchange chromatography
HMF	Hydroxymethylfurfural
I-fraction	Insoluble lignin in the hydrolyzate separated by centrifugation
KL	Klason lignin in wood and wood residues
MeGlcA	4-O-Methylglucuronic acid
NMR	Nuclear magnetic resonance spectroscopy
OA	Oxalic acid
PAD	Pulsed amperometric detection
P-factor	Prehydrolysis factor
PHK	Prehydrolysis kraft
RI	Refractive index
RT	Room temperature
S-fraction	Soluble lignin in the hydrolyzate remaining after centrifugation
TH	Total hydrolysis
TOC	Total organic carbon
TR	Thermal reactivation
WR	Wood residue
X	Xylose
XOS	Xylooligosaccharides

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Curriculum Vitae

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Education

1991-1995	Primary school, Vöcklabruck, Austria
1995-2003	Secondary school and High school Bundesgymnasium, Vöcklabruck, Austria
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2008	Research assistant at the Institute of Inorganic Chemistry – Center of Nanobionics and Photochemical Sciences (CNPS), Johannes Kepler University Linz, Austria
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Paper I

Gütsch, J.S., Sixta, H. (2011) Purification of Eucalyptus globulus water prehydrolyzates using the HiTAC process (high-temperature adsorption on activated charcoal).

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Purification of *Eucalyptus globulus* water prehydrolyzates using the HiTAC process (high-temperature adsorption on activated charcoal)

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Abstract

The implementation of biorefinery concepts into existing pulp and paper mills is a key step for a sustainable utilization of the natural resource wood. Water prehydrolysis of wood is an interesting process for the recovery of xylo-oligosaccharides and derivatives thereof, while at the same time cellulose is preserved to a large extent for subsequent dissolving pulp production. The recovery of value-added products out of autohydrolyzates is frequently hindered by extensive lignin precipitation, especially at high temperatures. In this study, a new high-temperature adsorption process (HiTAC process) was developed, where lignin is removed directly after the autohydrolysis, which enables further processing of the autohydrolyzates. The suitability of activated charcoals as a selective adsorbent for lignin under process-relevant conditions (150 and 170°C) has not been considered up to now, because former experiments showed decreasing efficiency of charcoal adsorption of lignin with increasing temperature in the range 20–80°C. In contrast to these results, we demonstrated that the adsorption of lignin at 170°C directly after autohydrolysis is even more efficient than after cooling the hydrolyzate to room temperature. The formation of lignin precipitation and incrustations can thus be efficiently prevented by the HiTAC process. The carbohydrates in the autohydrolysis liquor remain unaffected over a wide charcoal concentration range and can be further processed to yield valuable products.

Keywords: activated charcoal (AC); adsorption; autohydrolysis; *Eucalyptus globulus*; HiTAC process (high-temperature adsorption on activated charcoal); lignin; precipitate; prehydrolysis; xylo-oligosaccharides.

Introduction

Globally, the alkaline kraft process constitutes the principal pulping process. It accounts for 89% of chemical pulp production. Alkaline pulping processes, however, are not capable of selectively removing short-chain hemicelluloses as a prerequisite for the production of high-purity dissolving pulps (Sixta 2006). Autohydrolysis in water is the process of choice for the extraction of high-molecular-mass hemicelluloses from wood biomass for the production of a dissolving pulp, on the one hand, and of value-added products – such as food additives and pharmaceuticals from the hemicellulosic fraction – on the other hand. Thus, autohydrolysis may also contribute to the profitability of the pulping process (Garrote et al. 1999; Vázquez et al. 2000; Huang and Ramaswamy 2008).

One major challenge during autohydrolysis of wood is the partial dissolution of highly reactive lignin components. These components cause high turbidity of the autohydrolyzate and form resinous precipitates during heating and storage at high temperatures. The precipitates were specified as a highly condensed form of the colloidal dissolved lignin fraction (Leschinsky et al. 2007). Further processing of the autohydrolyzate such as heat recovery, isolation or hydrolysis of oligosaccharides as well as the separation of acetic acid and furanic compounds is impaired by extensive lignin precipitation. However, the formation of these insoluble precipitates cannot be avoided completely (Leschinsky 2009). In order to circumvent the precipitation problems and to simultaneously benefit from autohydrolysis, steam prehydrolysis is conducted in industrial practice. A disadvantage of this technique is the immediate neutralization of the hydrolyzates with cooking liquor, which renders impossible the isolation of hydrolyzed sugar components because of severe carbohydrate degradation and the small quantity of hydrolysis liquor (Wizani et al. 1994; Sixta 2006).

Thus, finding suitable technologies for the quantitative removal of the insoluble components and their precursors (soluble lignin) from autohydrolyzates is one of the prerequisites for the commercialization of water autohydrolysis for the parallel production of high-purity dissolving pulps and sugar-based by-products. The lignin separation step needs to be performed immediately after the drainage of the hydrolyzates from the reactor in order to completely avoid incrustation problems. The separation of lignin at temperatures exceeding 100°C has not been a research topic so far, however, lignin separation from hydrolyzates at ambient temperature has found some interest, especially in respect of the removal of inhibitors for fermentative purposes. Inhibitors in this context are lignin, lignin degradation products, and furanic compounds that are toxic to microorganisms in higher concentrations and therefore need to be removed prior to fermentation of the carbohydrate-containing liquors (Parajó et al. 1998; Cruz et al. 1999; Keller and Nguyen 2001; Villarreal et al. 2006; Mendes et al. 2009).

A large variety of purification methods has already been studied in this respect. Some adsorbent materials, such as ion exchange resins and activated charcoals, have proven to be applicable for the removal of lignin and sugar degradation products from carbohydrate-containing liquors (Moure et al. 2006). Even polymeric resins showed good efficiency in lignin removal, although they were not utterly selective as large amounts of carbohydrates were adsorbed, too (Schwartz and Lawoko 2010). Among the adsorbent materials, activated charcoals showed a rather good selectivity towards lignin and lignin degradation products. Parajó et al. (1996b) treated a neutralized acid hydrolyzate of *Eucalyptus globulus* wood with activated charcoal (hydrolyzate-to-charcoal ratio of 10 g g^{-1}, 24°C, 24 h) and could hence remove 75% of the lignin. Along with lignin removal, substantial co-adsorption of sugars was observed. Therefore, an optimal charcoal concentration was proposed, where sugar adsorption was still low. This concentration corresponds to a lignin removal of up to 65%, which agrees with results reported by Montané et al. (2006). The authors suggested that the selectivity of lignin retention is impaired with increasing lignin adsorption owing to the presence of lignin-carbohydrate linkages. The absolute capacity of an activated charcoal is generally characterized by its specific surface area and the distribution of pores on the charcoal surface. The role of micro- and mesopores of the activated charcoal on lignin adsorption is still under discussion. Montané et al. (2006) suggested that the best selectivity toward lignin adsorption was provided by microporous charcoals with small mesopore diameters, a low number of mesopores, and a low concentration of basic surface groups, while Marton et al. (2006) found no significant difference between the charcoals investigated.

In general, adsorption of lignin on activated charcoals is highest at low pH values, a condition typically met in untreated autohydrolyzates (Venkata Mohan and Karthikeyan 1997). Nevertheless, a neutralization step is often applied prior to adsorption, as neutral pH is required for subsequent fermentative treatments. In addition to neutralization, filtration and evaporation stages are often proposed to remove volatile compounds and to purify the hydrolyzates before an adsorption step (Parajó et al. 1996a; Canilha et al. 2004; Sepúlveda-Huerta et al. 2006; Villarreal et al. 2006). However, it is strongly recommended to remove the sticky and reactive lignin prior to the application of additional treatment steps, because lignin inevitably hampers the treatment by continuous precipitation.

The objective of this study was to develop a process for the removal of lignin and lignin degradation products from the autohydrolysis liquor immediately after its discharge from the pressurized reactor. In order to prevent excessive precipitation, the critical substances should be removed by adsorption on activated charcoal. The efficiency and selectivity of this HiTAC process (high-temperature adsorption on activated charcoal) should be investigated in detail. Within a temperature range of 20°C to 170°C, the effects of adsorption temperature, adsorption time and the type and amount of activated charcoal will be examined.

Materials and methods

Wood chips

Eucalyptus globulus wood chips from plantations in Uruguay were supplied by ENCE (Huelva, Spain). The chips were ground with a Retsch-type grinding cutting mill SM100 (Retsch GmbH, Haan, Germany) and fractionated. The fraction with particle sizes between 2.5 and 3.5 mm was collected and used for the prehydrolysis experiments. The dry content of the wood chips (82.9%) was measured after drying at 104°C until constant weight (48 h). The carbohydrate content and composition were analyzed after a two-stage total hydrolysis by high-performance anion exchange chromatography with pulsed amperometric detection (Sixta et al. 2001). Klason lignin and acid-soluble lignin were measured according to Tappi T222om 98 (Tappi 1998). The native wood composition is shown in Table 1.

Autohydrolysis

Autohydrolysis was carried out in a laboratory-scale Parr reactor 4560 series (Parr Instrument GmbH, Frankfurt am Main, Germany) station with a reactor volume of 450 ml, mechanical stirring and temperature control. Fifty grams of wood were placed inside the reactor. Deionized water was added to achieve a liquor-to-wood ratio of 5:1. The reactor was heated to 170°C within 30 min (minimum heating time), and the temperature was maintained until a prehydrolysis-factor (P-Factor) of 600 h (corresponding to approximately 60 min). The P-factor was calculated from the recorded temperature/time data according to Sixta (2006) based on an activation energy of 125.6 kJ mol^{-1}. The prehydrolyzate was subsequently separated from the wood residue by displacement with nitrogen to a preheated second reactor containing saturated steam with a temperature of 170°C following the protocol of Leschinsky (2009). The isothermal phase separation recovered all components that were dissolved in the prehydrolyzate at 170°C, particularly the components that were insoluble at lower temperatures. During this separation step, no temperature and pressure drop occurred. The experiments were split into reference and adsorption experiments. For reference measurements, the second reactor was filled with steam only, while for the adsorption experiments, activated charcoal was added.

Table 1 Composition of native *Eucalyptus globulus*.

Compounds	Amount (% o.d.w.)
Carbohydrates	
Glucan	39.9
Xylan	14.9
Rhamnan	0.1
Arabinan	0.3
Mannan	0.4
Galactan	1.3
Lignin	
Klason	23.6
Acid soluble	4.8
Ash	0.32

o.d.w., oven dried wood.

Reference experiments

In the reference experiments the hydrolyzates were subjected to a temperature treatment at 170°C for 0, 20, 40 and 80 min after isothermal phase separation. Then, the reactors were cooled to room temperature with ice-water. Precipitates that had built up during this treatment on the equipment were solubilized in 0.1 M NaOH with short heating to over 100°C and were quantified via standard total organic carbon (TOC) measurements.

Adsorption experiments

Sources of charcoal: Sigma decolorizing charcoal, Norit® granular charcoal (purchased from Sigma-Aldrich, St. Louis, MO, USA) and activated coke HOC Super (kindly supplied by Rheinbauer Brennstoff GmbH, Frechen, Germany). Norit® granular charcoal was ground, while the other charcoal samples were used as supplied. The activated charcoal concentration is given as the ratio to the liquid phase during prehydrolysis in (g l^{-1}). For adsorption experiments at 170°C the second reactor was held at 170°C; for adsorption experiments at 150°C, the batch was cooled with the reactor's internal cooling system immediately after liquid transfer from the first reactor. The temperature was maintained until the required adsorption time was accomplished. After the adsorption, the reactor was immediately cooled down to below 40°C with ice-water. Adsorption time of 0 min represents the minimal adsorption time possible to record. The minimum adsorption time at 170°C is estimated to be <2 min, followed by a cooling time to below 40°C of 10–15 min. Adsorption at 20°C was conducted after isothermal liquid transfer and ice cooling. The adsorbent was separated from the prehydrolyzate via vacuum filtration using a 0.45-μm membrane.

Analytical methods

Lignin and turbidity analysis were conducted immediately after the prehydrolysis experiments. The samples were then stored at 4°C. Lignin content was analyzed via [ultraviolet/visible light spectroscopy (UV/VIS-spectrometry)] (absorption coefficient of 110 l g^{-1} cm^{-1} at 205 nm according to Tappi um-250, Tappi 1991). Turbidity was measured on a Hach 2100P turbidimeter (Hach Lange GmbH, Düsseldorf, Germany). Furfural and hydroxymethylfurfural (HMF) were quantified via high-performance liquid chromatography (HPLC) on a Hypersil ODS column (Thermo Scientific, Waltham, MA, USA) with UV detection at 277 nm with 14% (v/v) acetonitrile as eluent at a temperature of 65°C. Acetic acid was determined via HPLC on a Rezex ROA column (Phenomenex, Torrance, CA, USA) with refractive index (RI) and UV detection and 0.005 M H_2SO_4 as eluent at a temperature of 65°C. The carbohydrate content and the composition of the samples were analyzed before and after a two-stage total hydrolysis with sulfuric acid by high-performance anion exchange chromatography with pulsed amperometric detection (Sixta et al. 2001). Size exclusion chromatograms (SEC) were obtained on a PSS MCX 1000 [Polymer Standards Service GmbH (PSS), Mainz, Germany] (8×300) column coupled with RI detection and 0.1 M NaOH as eluent. Brunauer Emmett Teller adsorption isotherm (BET) was measured on a BELsorp mini II (BEL Inc., Osaka, Japan) according to Brunauer et al. (1938) and International Union for pure and applied chemistry (IUPAC) recommendations (Rouquerol et al. 1994). Pore distributions were plotted in terms of the BHJ- and the MP-plot for meso- and micropores, respectively. Non-linear regression was analyzed by means of the Statgraphics Centurion XV software. The ash content of the activated charcoals was measured according to DIN 38 409 H1-3 (Deutsche-Norm 1987) at a temperature of 850°C. The ash content of the activated charcoals and the pH in water at a concentration of 50 g l^{-1} are shown in Table 2.

Table 2 BET surface area, pH, and ash content of the activated charcoals investigated.

Type of activated charcoal	BET (m^2 g^{-1})	pH	Ash (%)
Sigma decolorizing	880	6.7	1.1
Norit® (Sigma)	560	6.0	12
HOC Super	280	11.2	8.7

Results and discussion

Reference experiments

During autohydrolysis, mainly the xylan in the wood is degraded and solubilized in the aqueous phase, whereas the cellulose is depolymerized – depending on prehydrolysis intensity – but practically no water-soluble fractions are formed. The main components of the crude autohydrolyzate are oligomeric and monomeric sugars (25.2 g l^{-1}), mainly xylose (20.5 g l^{-1} xylose corresponding to 11.3% o.d.w.) and <1 g l^{-1} of glucose (0.5% o.d.w.). 68% of the xylose in solution was still in oligomeric form due to the rather mild conditions of autohydrolysis. Additionally, the carbohydrate degradation products furfural and hydroxymethylfurfural (HMF) as well as acetic acid derived from the hydrolysis of the acetyl groups attached to the xylan backbone were detected in the autohydrolyzate (1166, 113 and 2814 mg l^{-1}, respectively). Parallel to sugar dissolution from wood, some lignin also solubilizes in the hot hydrolyzate. A part of it precipitates upon cooling. The total lignin in the hydrolyzate accounts for 5.6% o.d.w. (10.1 g l^{-1} in hydrolyzate), 30% thereof can be separated by centrifugation. If the crude hydrolyzate is further exposed to the reaction temperature of 170°C, the oligomeric sugars are hydrolyzed to monosugars and subsequently dehydrated to furanic compounds in an extent depending on the treatment intensity. Additionally, a drop in lignin concentration was observed with increasing treatment time (Table 3), which can be attributed to the formation of incrustations due to polycondensation reactions (Leschinsky et al. 2008). These sticky incrustations lead to serious problems in the processability of autohydrolyzates because they contribute to scaling in all the downstream equipment, especially in the heat-exchanging devices.

Influence of activated charcoal

The addition of activated charcoal (AC), even in amounts far lower than those recommended in the literature (minimum 8 g AC per litre hydrolyzate versus 100 g AC per kg hydrolyzate according to Parajó et al. 1996b), could prevent the formation of incrustations efficiently. Adsorption time had only a minor effect on lignin adsorption at 170°C (Table 4). As sugar decomposition at 170°C started to be significant when exceeding 20 min of treatment time, the adsorption time was set to 20 min for further experiments.

Table 3 Reference experiments: composition of autohydrolyzates after temperature treatment at 170°C.

Compounds	Concentration of the compounds (mg l^{-1}) at different reaction times (min)			
	0	20	40	80
Lignin	10 114	9680	7546	6870
Sugar total[a]	25 225	23 368	20 949	17 742
Sugar oligo[b]	16 090	13 119	9685	4616
Xylose oligo[b]	13 945	11 212	8121	3489
Xylose mono[c]	6557	7664	8678	10 207
Glucose oligo[b]	630	515	450	358
Glucose mono[c]	274	293	338	497
Galactose oligo[b]	638	525	433	246
Galactose mono[c]	1196	1191	1180	1287
Furfural	1166	1555	2304	4257
HMF	113	172	237	426
Acetic acid	2814	3083	3743	4743
Incrustation[d]	–	430	2570	3240

[a] After total hydrolysis.

[b] Oligomeric fraction: difference in sugar content before and after total hydrolysis.

[c] Before total hydrolysis.

[d] Incrustations from the reactor dissolved in NaOH.

The turbidity of an aqueous system correlates with the amount of colloidal matter in solution, indicating an increase in insolubles with rising turbidity. This measuring principle can be adopted for the autohydrolysis liquor to track the concentration of colloidal lignin compounds causing the formation of sticky precipitates. Crude autohydrolyzates exhibited a turbidity of more than 10 000 NTU. Vacuum filtration, using a 0.45 μm membrane, still resulted in a turbidity higher than 1000 NTU indicating an insufficient removal of the colloidal lignin compounds, while the treatment with the minimal amount of AC resulted in a turbidity of 25 NTU only. An increase in AC concentration lowers turbidity to about 10 NTU. This turbidity value remained constant during a period of more than 3 weeks, stored at room temperature or 4°C, indicating no further lignin precipitation over time as confirmed by lignin content measurements. With the highest AC concentration in the hydrolyzate tested, 48 g l^{-1}, the lignin content in the hydrolyzate decreased by 96% (Table 5, Figure 1). Carbohydrates were not affected up to AC concentrations of 24 g l^{-1} corresponding to a lignin removal of 85%. However, at an AC concentration of 48 g l^{-1}, a concomitant adsorption of 19% of the carbohydrates, mainly present in their polymeric form, occurred (Table 5). The same tendencies were found by size exclusion chromatography (SEC). SECs of the crude hydrolyzates showed a bimodal molecular weight distribution (Figure 2). The low-molecular-weight peak is considered as monomeric sugars mainly, the higher-molecular-weight peak is composed of lignin and oligomeric sugars. With increasing charcoal concentration, the UV-active lignin is constantly removed and accounts for the reduction of the high-molecular-weight peak for the most part. UV detection showed a bimodal molecular weight distribution of lignin compounds, where lignin with a higher molecular mass is removed prior to low-molecular-mass lignin.

Table 4 Composition of the hydrolyzates after treatment with activated charcoal (AC) with BET 880 m^2 g^{-1} at 170°C.

Concentration and adsorption time of AC		Concentration of	
		Lignin	Sugar
(g l^{-1})	(min)	(mg l^{-1})	(mg l^{-1})
8	0[a]	5674	23 685
8	20	5634	23 712
8	40	5099	20 722
8	80	5326	17 170
12	20	4391	23 631
12	40	4215	21 421
12	80	4847	14 021

[a] Minimum adsorption time.

The C_5- and C_6-sugar dehydration products furfural and HMF were increasingly removed from autohydrolysis liquor with rising charcoal concentrations. At the maximum charcoal concentration investigated (48 g l^{-1}), 85% of furfural and 72% of HMF were removed from the autohydrolysis liquor. Acetic acid concentration was not reduced by AC, but was rather significantly increased at high AC concentrations.

A theoretically possible catalysis of the cleavage of acetyl groups from the xylan backbone by activated charcoal and the concomitant release of free acetic acid into the hydrolyzate needs further investigation. Anyway, a release of free acetic acid would promote further hydrolysis of the oligosaccharides to monomeric sugars and would therefore explain the increase in monomeric sugars which is presented in Figure 3.

An interesting field of application for water prehydrolyzates is the fermentative and enzymatic conversion of the carbohydrates (xylan, xylooligosaccharides and xylose) to xylitol, bioethanol, and other fermentation products. Lignin, furfural, and HMF are inhibitors for most of the enzymes in question. The amounts of lignin, furfural, and HMF in *E. globulus* water prehydrolyzates, subjected to the HiTAC process, are at a sufficiently low level for fermentation processes (Parajó et al. 1998; Cruz et al. 1999; Keller and Nguyen 2001; Villarreal et al. 2006; Mendes et al. 2009).

Adsorption isotherms

Lignin adsorption on activated charcoal is fairly efficient at 170°C (Figure 1); adsorption at 170°C is even better than at room temperature. The measurement of the exact equilibrium adsorption time of lignin in autohydrolyzate at high temperatures is not possible due to the high amount of side reactions of carbohydrates and furfural. Nevertheless, it was shown that the lignin concentration in the hydrolyzate did not decrease steadily with adsorption times exceeding 20 min. Therefore, an adsorption time of 20 min was chosen for the adsorption experiments. Adsorption equilibrium at room temperature is known to be attained only after several hours of adsorption time (Venkata Mohan and Karthikeyan 1997).

The adsorption behavior of the hydrolysis lignin can be approximated by isotherms of type I, although there is a

Table 5 Composition of prehydrolyzates after 20 min adsorption onto AC (BET 880 m^2 g^{-1}) at 170°C.

	Concentration of the compounds (mg l^{-1}) after treatment with AC concentrations (mg l^{-1})						
Compounds	0	8	12	20	24	32	48
Lignin	9680	5634	4391	2972	1559	921	376
Sugar total[a]	23 368	23 711	23 631	23 398	22 184	20 732	18 983
Sugar oligo[b]	13 119	12 680	13 108	13 661	11 574	10 481	6941
Xylose oligo[b]	11 212	10 810	11 218	11 609	9678	8965	5236
Xylose mono[c]	7664	8231	7796	7190	7918	7595	9348
Glucose oligo[b]	515	588	579	585	572	436	406
Glucose mono[c]	293	326	324	274	335	293	434
Galactose oligo[b]	525	544	581	614	512	467	437
Galactose mono[c]	1191	1283	1275	1205	1252	1242	1342
Furfural	1555	1477	1167	1068	720	333	237
HMF	172	153	127	137	118	71	49
Acetic acid	3083	3341	3531	3557	3496	3182	4175
Incrustation[d]	430	–	–	–	–	–	–

[a] After total hydrolysis.

[b] Oligomeric fraction: difference in sugar content before and after total hydrolysis.

[c] Before total hydrolysis.

[d] Incrustations from the reactor dissolved in NaOH.

slight tendency of increasing coverage at higher lignin concentrations (Figure 4). High surface coverage at high concentrations indicates the formation of multilayers at the adsorbent surface. However, within the concentration range investigated this could not be unambiguously confirmed. The study of higher lignin concentrations or lower activated charcoal concentrations was not possible owing to the formation of lignin incrustations at lower AC concentrations at high temperatures. Type I isotherms can be modelled according to the theories of Freundlich and Langmuir. The Langmuir isotherm describes adsorption in a monomolecular layer, where adsorption of a particle is independent of the degree of surface coverage according to equation 1:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot \beta} + \frac{C_e}{Q_0} \tag{1}$$

where q_e is the amount of lignin adsorbed per unit mass of activated carbon (mg g^{-1}), C_e is the equilibrium concentration of lignin in solution (mg l^{-1}), Q_0 is the maximum lignin uptake per unit mass of carbon (mg g^{-1}), and β is the Langmuir constant (l mg^{-1}).

The Freundlich adsorption isotherm additionally relates the concentration of the solute on the surface of the adsorbent, to the concentration of the solute in the liquid phase in a logarithmical relationship. The Freundlich equation can be written as:

$$q_e = k_f \cdot C_e^{1/n} \tag{2}$$

where q_e and C_e correspond to the Langmuir terms, k_f is the Freundlich constant related to the adsorption capacity [mg g^{-1} (mg l^{-1})^n], and n is a dimensionless empirical parameter representing the heterogeneity of the surface.

Both, Freundlich and Langmuir isotherm models, gave good correlation with the measured lignin adsorption data.

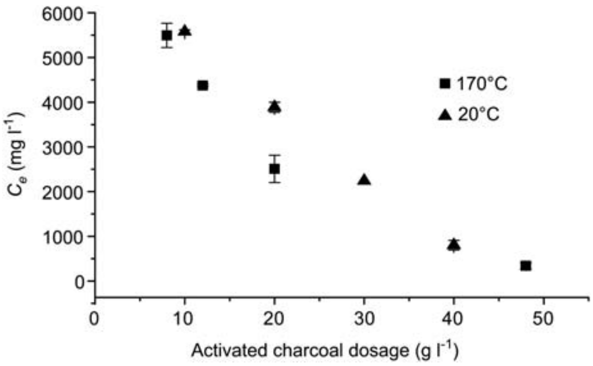

Figure 1 Lignin adsorption at 20°C and 170°C: lignin concentration as a function of AC dosage. C_e, equilibrium concentration of lignin in solution.

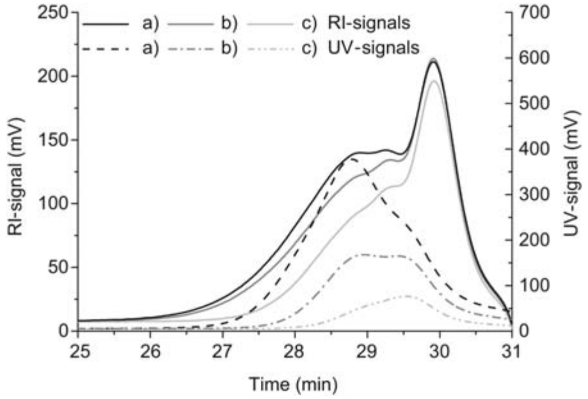

Figure 2 Size exclusion chromatograms of the autohydrolyzates after adsorption on (a) 12 g l^{-1}, (b) 24 g l^{-1} and (c) 48 g l^{-1} activated charcoal (BET 880 m^2 g^{-1}) for 20 min at 150°C.

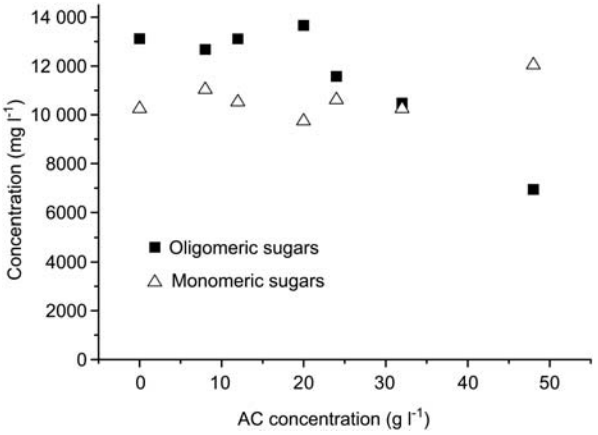

Figure 3 Oligomeric and monomeric sugars as a function of AC dosage (adsorption parameters: 20 min, 170°C).

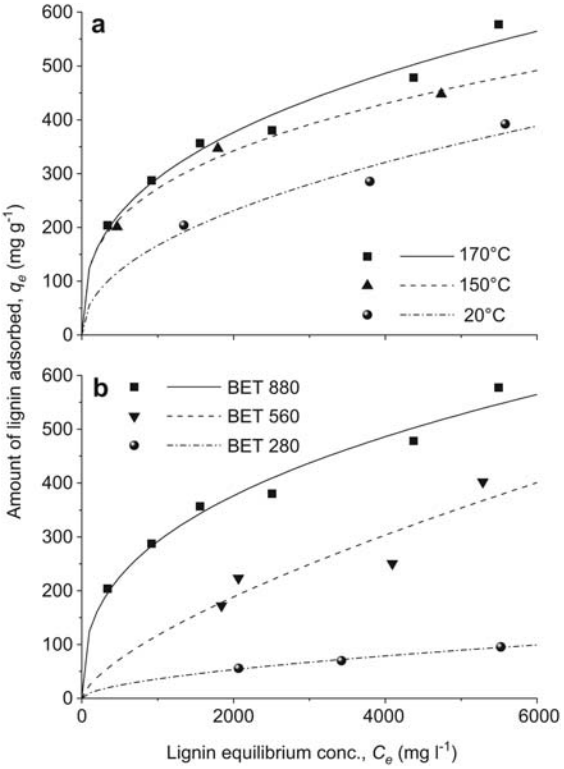

Figure 4 Freundlich isotherms (curves) and experimental adsorption data (individual points) of lignin on activated charcoal. q_e amount of lignin adsorbed per unit mass of AC, C_e equilibrium concentration of lignin in solution. (a) BET 880 m^2 g^{-1} at 20, 150 and 170°C. (b) BET surface area of 880, 560 and 260 m^2 g^{-1} for 20 min at 170°C.

Non-linear regression was performed in order to attain the Freundlich and Langmuir coefficients (Table 6). The Freundlich model showed a slightly better fit (mean R^2 0.96) compared to the Langmuir model (mean R^2 0.92). Figure 4a shows the Freundlich isotherms for three different adsorption temperatures (20, 150, 170°C). Notably, the amount of lignin adsorbed per unit mass of adsorbent (q_e) significantly increased at elevated temperatures, indicating more efficient adsorption. We therefore suggest that the lignin in solution at 170°C exhibits a different structure than at room temperature or even is in liquid state. The arrangement of hydrophilic and hydrophobic groups in this state might favour the adsorption onto activated charcoal. Validation of these assumptions will require further research in this area. Furthermore, we propose that the adsorption of lignin on AC at high temperatures follows a chemisorption process as indicated in the literature (Venkata Mohan and Karthikeyan 1997) and in our own preliminary desorption experiments with limited success. Elevated temperatures might provide the activation energy required for a chemisorptive process. We further suspect a change in the adsorption mechanism at temperatures beyond 100°C, as Parajo found that in the range between 20 and 60°C the adsorption efficiency decreased significantly with increasing temperature (Parajó et al. 1996a)

Due to the long adsorption times at 20°C, it can be assumed that no significant lignin adsorption occurred during the cooling phase. Furthermore, after 80 min of adsorption at 170°C and a charcoal amount exceeding 12 g l^{-1} no incrustations were formed (Table 4). Thus, lignin was not available for condensation reactions. This also indicates that the lignin was already adsorbed before cooling. Reference measurements without activated charcoal at the same conditions, however, yielded an amount of incrustations higher than 3.2 g l^{-1}.

Effect of activated charcoal type

Three activated charcoals with BET surface areas of 280, 560 and 880 m^2 g^{-1} were tested for lignin adsorption. The adsorption behavior of the different charcoals was modelled in terms of Freundlich and Langmuir isotherms (Figure 4b, Table 6), whereby the fit of the former was significantly better (mean R^2 of 0.92 compared to 0.88). The charcoals showed small meso- and micropore diameters (Figure 5). The volume of mesopores was almost equal for the charcoals with a BET surface area of 560 and 880 m^2 g^{-1}. The micropore volume, however, was much higher for the AC of BET 880 m^2 g^{-1}. The AC of BET 280 m^2 g^{-1} exhibited only small volumes of meso- and micropores. In terms of lignin adsorption, a decrease of the BET surface from 880 to 560 m^2 g^{-1} resulted in a 50% higher demand of AC to yield a comparable lignin reduction (Table 7). A further decrease of the BET surface area to 280 m^2 g^{-1} required six times the amount

Table 6 Freundlich and Langmuir coefficients calculated by non-linear regression.

Temp. (°C)	BET (m^2 g^{-1})	Freundlich			Langmuir		
		k	1/n	R^2	Q	β	R^2
170	880	22.83	0.37	0.97	617.70	1052.5	0.89
150	880	28.00	0.33	0.99	512.55	767.8	0.99
20	880	6.36	0.47	0.93	530.43	2456.1	0.88
170	560	1.02	0.69	0.81	884.41	7498.0	0.79
170	280	0.72	0.57	0.99	174.25	4700.1	0.97

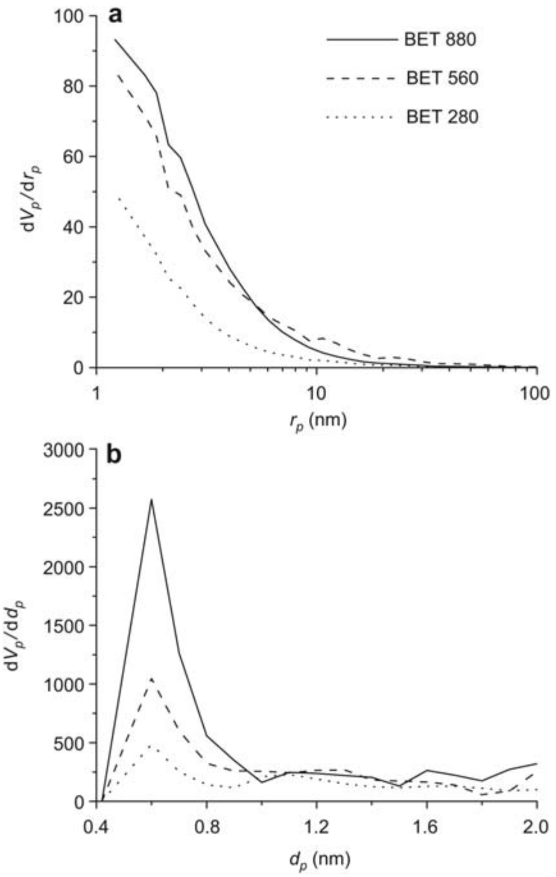

Figure 5 (a) Mesopore and (b) micropore distribution of the three activated charcoals with BET surface areas of 880, 560 and 280 m^2 g^{-1}. (r_p, pore radius; d_p, pore diameter; V_p, pore volume.)

of AC to achieve the equivalent adsorption efficiency. Taking into account the total surface area of the adsorption system as the surface area (m^2 g^{-1}) of the AC times the amount of AC (g l^{-1}), it can be seen that similar total surface areas are needed for the two charcoals of high microporosity (AC with BET 560 and 880 m^2 g^{-1}). For the charcoal of minor microporosity (AC with BET 280 m^2 g^{-1}) almost twice the total surface area is needed for similar lignin removal. Thus, not only the total surface area is a criterion for lignin adsorption, but also microporosity and assumingly surface functionalities. This is in agreement with the findings of Montané et al. (2006), who found increased lignin adsorption for highly microporous charcoals with small mesopore diameters. A potential effect of the ash content and the alkalinity of the ACs on the lignin adsorption is possibly superimposed by the high differences in BET surface area. The alkalinity of the AC might affect the stability of carbohydrates during the adsorption process.

Table 7 Influence of BET surface area on lignin adsorption (170°C, 20 min).

BET surface (m^2 g^{-1})	AC (g l^{-1})	Lignin (mg l^{-1})
880	8	5634
880	20	2972
880	48	376
555	24	4094
555	36	2063
555	48	1842
280	48	5525
280	96	3424
280	144	2068

Conclusions

Adsorption of lignin and lignin degradation products from autohydrolyzates on activated charcoals at prehydrolysis temperature is a suitable method for the prevention of scaling. The so-called HiTAC process exhibits a fairly good selectivity towards lignin adsorption without concomitant adsorption of carbohydrates up to a lignin removal of 85% at 170°C. At higher charcoal concentrations oligomeric sugars are increasingly adsorbed, while monomeric sugars remain unaffected. The carbohydrate dehydration products, furfural and HMF, are removed during the AC treatment to a concentration sufficiently low which allows an uninhibited fermentation of the hydrolyzate. The equilibrium adsorption time is reached within a rather short period of time. Surprisingly, it could be shown that adsorption is significantly more efficient at autohydrolysis temperature (150 and 170°C) than at room temperature, which is advantageous for purifying the hydrolyzate during its discharge from the digester. The choice of an activated charcoal of high microporosity and surface area is indispensable for a successful implementation in commercial practice. It was demonstrated that the addition of activated charcoal to the hydrolyzate at reaction temperature is very effective and selective in the removal of reactive lignin preventing the formation of precipitates. Clearly, a cost-effective regeneration process for the charcoal is needed for a commercial realization. Thus, it is our goal to develop an appropriate recycling strategy for the exhausted charcoal.

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Paper II

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THE HITAC-PROCESS (HIGH TEMPERATURE ADSORPTION ON ACTIVATED CHARCOAL) – NEW POSSIBILITIES IN AUTOHYDROLYSATE TREATMENT

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Water prehydrolysis of wood is an interesting process for the recovery of xylooligosaccharides and derivatives thereof, while at the same time cellulose is preserved to a large extent for subsequent dissolving pulp production. The recovery of value-added products out of autohydrolysates is frequently hindered by extensive lignin precipitation, especially at high temperatures. In this study, a new high temperature adsorption process (HiTAC process) was developed, where lignin is removed directly after the autohydrolysis, which enables further processing of the autohydrolysates. The suitability of activated charcoals as a selective adsorbent for lignin under process relevant conditions (150 and 170 °C) has not been considered up to now, because former experiments showed decreasing efficiency of the adsorption of lignin onto activated charcoals with increasing temperature in the range of 20 – 80 °C. In contrast to these results, we demonstrated that the adsorption of lignin at 170 °C directly after autohydrolysis is even more efficient than after cooling the hydrolysate to room temperature. The formation of lignin precipitation and incrustations can thus be efficiently prevented by the HiTAC process. The carbohydrates in the autohydrolysis liquor remain unaffected over a wide charcoal concentration range and can be further processed to yield valuable products.

Keywords: activated charcoal (AC), adsorption, autohydrolysis, desorption, *Eucalyptus globulus*, HiTAC process (high temperature adsorption on activated charcoal), lignin, precipitation, prehydrolysis, xylooligosaccharides

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Introduction

Globally, the alkaline kraft process constitutes the principal pulping process. It accounts for 89 % of the chemical pulp production. Alkaline pulping processes, however, are not capable of selectively removing hemicelluloses as a prerequisite for the production of high-purity dissolving pulps [1]. Autohydrolysis in water is the process of choice for the extraction of the hemicelluloses from wood biomass for the subsequent production of a dissolving pulp. The extracted hemicelluloses are an interesting feedstock for food additives and pharmaceuticals. Thus, autohydrolysis may contribute to the profitability of the pulping process [2-4]. One major challenge during autohydrolysis of wood is the partial dissolution of highly reactive lignin components. These components cause high turbidity of the autohydrolysate and form resinous precipitates during heating and storage at high temperatures. The precipitates were specified as a highly condensed form of the colloidal dissolved lignin fraction [5]. Further processing of the autohydrolysate such as heat recovery, isolation or hydrolysis of oligosaccharides as well as the separation of acetic acid and furanic compounds is impaired by extensive lignin precipitation. However, the formation of these insoluble precipitates cannot be avoided completely [6]. In order to circumvent the precipitation problems and to simultaneously benefit from autohydrolysis, steam prehydrolysis is conducted in industrial practice. A disadvantage of this technique is the immediate neutralisation of the hydrolysates with cooking liquor, which renders impossible the isolation of hydrolysed sugar components because of severe carbohydrate degradation and the small quantity of hydrolysis liquor [1, 7].

Thus, finding suitable technologies for the quantitative removal of the insoluble components and their precursors (soluble lignin) from autohydrolysates is one of the prerequisites for the commercialization of water autohydrolysis for the parallel production of high purity dissolving pulps and sugar-based by-products. The lignin separation step needs to be performed immediately after the drainage of the hydrolysates from the reactor in order to completely avoid incrustation problems. The separation of lignin at temperatures exceeding 100 °C has not been a research topic so far, however, lignin separation from hydrolysates at ambient temperature has found some interest, especially in respect of the removal of inhibitors for fermentative purposes. Inhibitors in this context are lignin, lignin degradation products, and furanic compounds that are toxic to microorganisms in higher concentrations and therefore need to be removed prior to fermentation of the carbohydrate containing liquors [8-12].

A large variety of purification methods has already been studied in this respect. Some adsorbent materials, such as ion exchange resins and activated charcoals, have proven to be applicable for the removal of lignin and sugar degradation products from carbohydrate containing liquors [13]. Even polymeric resins showed good efficiency in lignin removal, although they were not utterly selective as large amounts of carbohydrates were adsorbed, too [14]. Among the adsorbent materials, activated charcoals showed a rather good selectivity towards lignin and lignin degradation products [15, 16]. However, along with lignin removal, substantial co-adsorption of sugars can be observed. Therefore, an optimal charcoal concentration was proposed, where sugar adsorption was still low.

In general, adsorption of lignin on activated charcoals is highest at low pH values, a condition typically met in untreated autohydrolysates [17]. Nevertheless, a neutralisation step is often applied prior to adsorption, as neutral pH is required for subsequent fermentative treatments. In addition to neutralization, filtration and evaporation stages are often proposed to remove volatile compounds and to purify the hydrolysates before an adsorption step [8, 18-20]. However, it is strongly recommended to remove the sticky and reactive lignin prior to the application of additional treatment steps, because lignin inevitably hampers the treatment by continuous precipitation.

The objective of this study was to develop a process for the removal of lignin and lignin degradation products from the autohydrolysis liquor immediately after its discharge from the pressurized reactor. In order to prevent excessive precipitation, the critical substances should be removed by adsorption on activated charcoal. The efficiency and selectivity of this HiTAC process (high temperature adsorption on activated charcoal) should be investigated in detail. Within a temperature range of 20 °C to 170 °C, the effects of adsorption temperature, adsorption time and the type and amount of activated charcoal will be examined. Furthermore desorption of the lignin components from the charcoal will be investigated, in order to reuse the charcoal.

Material and Methods

Wood chips

Eucalyptus globulus wood chips from plantations in Uruguay were supplied by ENCE (Huelva, Spain). The chips were ground with a Retsch-type grinding mill and fractionated. The fraction with particle sizes between 2.5 and 3.5 mm was collected and used for the prehydrolysis experiments. The dry content of the wood chips (82.9 %) was measured after drying at 104 °C until constant weight (48 h). The carbohydrate content and composition were analyzed after a two-stage total hydrolysis by high performance anion exchange chromatography with pulsed amperometric detection [21]. Klason lignin and acid soluble lignin were measured according to Tappi T222om 98 [22].

Autohydrolysis

Autohydrolysis was carried out in a lab-scale Parr reactor station with a reactor volume of 450 ml, mechanical stirring and temperature control. 50 g of wood were placed inside the reactor. Deionised water was added to achieve a liquor-to-wood ratio of 5:1. The reactor was heated up to 170 °C within 30 min (minimum heating time), the temperature was maintained until a prehydrolysis-factor (P-Factor) of 600 h (corresponding to approximately 60 min). The P-factor was calculated from the recorded temperature/time data according to Sixta [1] based on an activation energy of 125.6 kJ mol^{-1}. The prehydrolysate was subsequently separated from the wood residue by displacement with nitrogen to a preheated second reactor containing saturated steam with a temperature of 170 °C following the protocol of Leschinsky [6]. The isothermal phase separation recovered all components that are dissolved in the prehydrolysate at 170 °C, particularly the components that are insoluble at lower temperatures. During this separation step, no temperature and pressure drop occurred. The experiments were split into reference and adsorption experiments. For reference measurements, the second reactor was filled with steam only, while for the adsorption experiments, activated charcoal was added. The corresponding reactor scheme is shown in Figure 1.

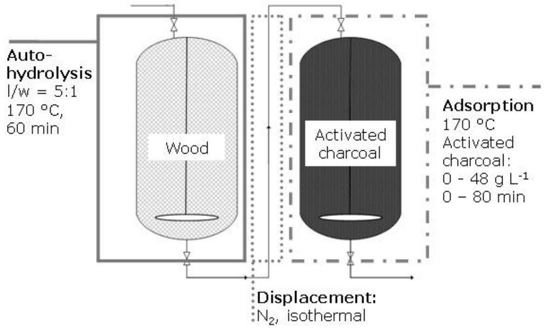

Figure 1. Autohydrolysis' reactor system.

Reference experiments

In the reference experiments the hydrolysates were subjected to a temperature treatment at 170 °C for 0, 20, 40 and 80 min after isothermal phase separation. Then, the reactors were cooled to room temperature with ice water. Precipitates that had built up during this treatment on the equipment were solubilised in 0.1 M NaOH with short heating to over 100 °C and were quantified via standard TOC measurements.

Adsorption experiments

Sources of charcoal: Sigma decolorizing charcoal, Norit® granular charcoal purchased from Sigma-Aldrich, Carbopal Gn-AZ from Donau Carbon and activated coke HOC Super, kindly supplied by Rheinbauer Brennstoff GmbH. Norit® granular charcoal was ground, while the other charcoal samples were used as supplied. The activated charcoal concentration is given as the ratio to the liquid phase during prehydrolysis in (g L^{-1}). For adsorption experiments at 170 °C the second reactor was held at 170 °C, for adsorption experiments at 150 °C, the batch was cooled with the reactor's internal cooling system immediately after liquid transfer from the first reactor. The temperature was maintained until the required adsorption time was accomplished. After the adsorption, the reactor was immediately cooled down to below 40 °C with ice water. Adsorption time of 0 min represents the minimal adsorption time possible to record. The minimum adsorption time at 170 °C is estimated to be less than 2 min, followed by a cooling time to below 40 °C of 10 - 15 min. Adsorption at 20 °C was conducted after isothermal liquid transfer and ice cooling. The adsorbent was separated from the prehydrolysate via vacuum filtration using a 0.45 µm membrane.

Table 1. BET surface area, pH and ash content of the activated charcoals.

Type of activated charcoal	BET / m^2 g^{-1}	pH	Ash / %
Carbopal Gn-AZ	1270	5.9	n.d.
Sigma decolorizing	880	6.7	1.1
Norit® (Sigma)	560	6.0	12
HOC Super	280	11.2	8.7

Desorption Experiments

1 g of spent activated carbon (adsorption paramenters: 20 g L^{-1} AC, adsorption at 170 °C, 20 min adsorption time, 410 mg lignin per g AC) was subjected to 5 mL of solvent [0.5 N NaOH, acetone/ water 5:1 (v/v), ethanol, acetic acid, DMSO] and shook overnight. AC was separated via a 0.45 µm filter and washed with 100 mL deionised water.

Analytical methods

Lignin and turbidity analysis were conducted immediately after the prehydrolysis experiments. The samples were then stored at 4 °C. Lignin content was analysed via UV/VIS-spectrometry (absorption coefficient of 110 L g^{-1} cm^{-1} at 205 nm according to Tappi um-250, [23]). Turbidity was measured on a Hach 2100P turbidimeter. Furfural and hydroxylmethyl-furfural (HMF) were quantified via HPLC on a Hypersil ODS column with UV detection at 277 nm with 14 % (v/v) acetonitrile as eluent at a temperature of 65 °C. Acetic acid was determined via HPLC on a Rezex ROA column with RI and UV detection and 0.005 M H_2SO_4 as eluent at a temperature of 65 °C. The carbohydrate content and the composition of the samples were analyzed before and after a two-stage total hydrolysis with sulphuric acid by high performance anion exchange chromatography with pulsed amperometric detection [21]. Size exclusion chromatograms (SEC) were obtained on a PSS MCX 1000 (8x300) column coupled with RI detection and 0.1 M NaOH as eluent. BET was measured on a BELsorp mini II from BEL Inc., Japan according to Brunauer *et al.* [24] and IUPAC recommendations [25]. Nonlinear regression was analysed by means of the Statgraphics Centurion XV software. The ash content of the ACs was measured according to DIN 38 409 H1-3 [26] at a temperature of 850 °C. The ash content of the activated charcoals and the pH in water at a concentration of 50 g L^{-1} are given in Table 1. Charcoal samples have been examined by high-resolution scanning electron microscopy after coating with a thin layer of Au/Pd at a 7000x magnification with a Hitachi S4000 SEM (FE-SEM) applying an acceleration voltage of 6 kV.

Results and discussion

Reference experiments

During autohydrolysis, mainly the xylan in the wood is degraded and solubilised in the aqueous phase, whereas the cellulose is depolymerised - depending on prehydrolysis intensity - but practically no water soluble fractions are formed. The main components of the crude autohydrolysate are oligomeric and monomeric sugars (25.2 g L^{-1}), mainly xylose (20.5 g L^{-1} xylose corresponding to 11.3 % odw) and less than 1 g L^{-1} of glucose (0.5 % odw). 68 % of the xylose in solution was still in oligomeric form due to the rather mild conditions of autohydrolysis. Additionally, the carbohydrate degradation products furfural and hydroxymethylfurfural (HMF) as well as acetic acid derived from the hydrolysis of the acetyl groups attached to the xylan backbone were detected in the autohydrolysate (1166, 113 and

2814 mg L^{-1}, respectively). Parallel to sugar dissolution from wood, some lignin also solubilises in the hot hydrolysate. A part of it precipitates upon cooling. The total lignin in the hydrolysate accounts for 5.6 % odw (10.1 g L^{-1} in hydrolysate), 30 % thereof can be separated by centrifugation. If the crude hydrolysate is further exposed to the reaction temperature of 170 °C, the oligomeric sugars are hydrolysed to monosugars and subsequently dehydrated to furanic compounds in an extent depending on the treatment intensity.

Table 2. Composition of the hydrolysates after activated charcoal (AC, BET 880 m^2 g^{-1}) treatment at 170 °C.

AC / g L^{-1}	**Adsorp. time** / min	**Lignin** / mg L^{-1}	**Total sugars** / mg L^{-1}
8	0*	5674	23685
	20	5634	23712
	40	5099	20722
	80	5326	17170
12	20	4391	23631
	40	4215	21421
	80	4847	14021

*minimum adsorption time

Additionally, a drop in lignin concentration was observed with increasing treatment time (Table 2) which can be attributed to the formation of incrustations due to polycondensation reactions [27]. These sticky incrustations lead to serious problems in the processability of autohydrolysates because they contribute to scaling in all downstream equipment, especially in the heat exchanging devices.

Influence of activated charcoal

The addition of activated charcoal (AC), even in amounts far lower than those recommended in the literature (minimum 8 g AC per litre hydrolysate versus 100 g AC per kg hydrolysate [15]), could prevent the formation of incrustations efficiently. Adsorption time had only a minor effect on lignin adsorption at 170 °C (Table 3). As sugar decomposition at 170 °C started to be significant when exceeding 20 min of treatment time, the adsorption time was set to 20 min for further experiments.

The turbidity of an aqueous system correlates with the amount of colloidal matter in solution indicating an increase in insolubles with rising turbidity. This measuring principle can be adopted for the autohydrolysis liquor to track the concentration of colloidal lignin compounds causing the formation of sticky precipitates. Crude autohydrolysates exhibited a turbidity of more than 10 000 NTU. Vacuum filtration, using a 0.45 µm membrane, still resulted in a turbidity higher than 1000 NTU indicating an insufficient removal of the colloidal lignin compounds, while the treatment with the minimal amount of AC (8 g L^{-1}) resulted in a turbidity of 23 NTU only. An increase in AC concentration lowers turbidity to below 10 NTU. This turbidity value remained constant during a period of more than three weeks, stored at room temperature or 4 °C, indicating no further lignin precipitation over time as confirmed by lignin content measurements. With the highest AC concentration in the hydrolysate tested, 48 g L^{-1}, the lignin content in the hydrolysate decreased by 96 % (Table 4). Carbohydrates were not affected up to AC concentrations of 24 g L^{-1} corresponding to a lignin removal of 85 %. However, at an AC concentration

Table 3. Reference experiments: Composition of autohydrolysates after temperature treatment at 170 °C.

Adsorp. time / min	**Lignin** / mg L^{-1}	**Xylose oligo**^{1} / mg L^{-1}	**Xylose mono**^{2} / mg L^{-1}	**Furfural** / mg L^{-1}	**HMF** / mg L^{-1}	**Acetic acid** / mg L^{-1}	**Incrust.**^{3} / mg L^{-1}
0	10114	13945	6557	1166	113	2814	–
20	9680	11212	7664	1555	172	3083	430
40	7546	8121	8678	2304	237	3743	2570
80	6870	3489	10207	4257	426	4743	3240

^{1} oligomeric fraction: difference in sugar content before and after total hydrolysis, ^{2} before total hydrolysis,
^{3} incrustations from the reactor equipment dissolved in NaOH

of 48 g L^{-1}, a concomitant adsorption of 19 % of the carbohydrates, mainly present in their polymeric form, occurred.

The same tendencies were found by size exclusion chromatography (SEC). SECs of the crude hydrolysates showed a bimodal molecular weight distribution (Figure 2). The low molecular weight peak is considered as monomeric sugars mainly, the higher molecular weight peak is composed of lignin and oligomeric sugars.

With increasing charcoal concentration, the UV active lignin is constantly removed and accounts for the reduction of the high molecular weight peak for the most part. UV detection showed a bimodal molecular weight distribution of lignin compounds, where lignin with a higher molecular mass is removed prior to low molecular mass lignin. The C_5- and C_6-sugar dehydration products furfural and HMF were increasingly removed from autohydrolysis liquor with rising charcoal concentrations. At the maximum charcoal concentration investigated (48 g L^{-1}), 85 % of furfural and 72 % of HMF were removed from the autohydrolysis liquor. Acetic acid concentration was not reduced by AC, but was rather significantly increased at high AC concentrations.

A theoretically possible catalysis of the cleavage of acetyl groups from the xylan backbone by activated charcoal and the concomitant release of free acetic acid into the hydrolysate needs further investigation. Anyway, a release of free acetic acid would promote further hydrolysis of the oligosaccharides to monomeric sugars and would therefore explain the increase in monomeric sugars (Table 4).

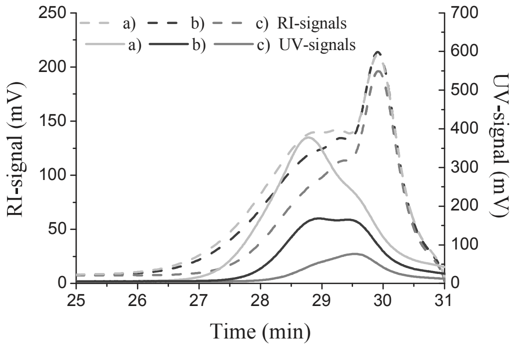

Figure 2. Size exclusion chromatograms of the autohydrolysates after adsorption on a) 12 g L^{-1}, b) 24 g L^{-1}) and c) 48 g L^{-1} activated charcoal (BET 880 m^2 g^{-1}) for 20 min at 150 °C.

An interesting field of application for water prehydrolysates is the fermentative and enzymatic conversion of the carbohydrates (xylan, xylooligosaccharides and xylose) to xylitol, bioethanol, and other fermentation products. Lignin, furfural and HMF are inhibitors for most of the enzymes in question. The amounts of lignin, furfural and HMF in *E. globulus* water prehydrolysates, subjected to the HiTAC process, are at a sufficiently low level for fermentation processes [8-12].

Adsorption isotherms

Lignin adsorption on activated charcoal is fairly efficient at 170 °C, adsorption at 170 °C is even better than at room temperature. The measurement of the exact equilibrium adsorption time of lignin in autohydrolysate at high temperatures is not possible due to the high amount of side reactions of carbohydrates and furfural. Nevertheless, it was shown that the lignin concentration in the hydrolysate did not

Table 4. Composition of prehydrolysates after 20 min adsorption onto activated charcoal (BET 880 m^2 g^{-1}) at 170 °C.

AC[1]	**Lignin**	**Sugar total**[2]	**Sugar oligo**[3]	**Xylose oligo**[3]	**Xylose mono**[4]	**Glucose oligo**[3]	**Glucose mono**[4]	**Furfural**	**HMF**	**Acetic acid**	**Incrust.**[5]
/g l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}	/mg l^{-1}
0	9680	23368	13119	11212	7664	515	293	1555	172	3083	430
8	5634	23711	12680	10810	8231	588	326	1477	153	3341	-
12	4391	23631	13108	11218	7796	579	324	1167	127	3531	-
20	2972	23398	13661	11609	7190	585	274	1068	137	3557	-
24	1559	22184	11574	9678	7918	572	335	720	118	3496	-
32	921	20732	10481	8965	7595	436	293	333	71	3182	-

[1] Activated charcoal, [2] after total hydrolysis, [3] oligomeric fraction: difference in sugar content before and after total hydrolysis [4] before total hydrolysis, [5] incrustations from the reactor equipment dissolved in NaOH

decrease steadily with adsorption times exceeding 20 min. Therefore, an adsorption time of 20 min was chosen for the adsorption experiments. Adsorption equilibrium at room temperature is known to be attained only after several hours of adsorption time [17].

The adsorption behaviour of the hydrolysis lignin can be approximated by isotherms of type I, although there is a slight tendency of increasing coverage at higher lignin concentrations (Figure 3). High surface coverage at high concentrations indicates the formation of multilayers at the adsorbens' surface. However, within the concentration range investigated, this couldn't be unambiguously confirmed. The study of higher lignin concentrations or lower activated charcoal concentrations was not possible, owing to the formation of lignin incrustations at lower AC concentrations at high temperatures. Type I isotherms can be modelled according to the theories of Freundlich and Langmuir. The Langmuir isotherm describes adsorption in a monomolecular layer, where adsorption of a particle is independent of the degree of surface coverage according to equation 1:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 \cdot \beta} + \frac{C_e}{Q_0} \qquad (1)$$

where q_e is the amount of lignin adsorbed per unit mass of activated carbon (mg g^{-1}), C_e is the equilibrium concentration of lignin in solution (mg L^{-1}), Q_0 is the maximum lignin uptake per unit mass of carbon (mg g^{-1}), and β is the Langmuir constant (L mg^{-1}).

The Freundlich adsorption isotherm additionally relates the concentration of the solute on the surface of the adsorbent to the concentration of the solute in the liquid phase in a logarithmical relationship. The Freundlich equation can be written as:

$$q_e = k_f \cdot C_e^{\,1/n} \qquad (2)$$

where q_e and C_e correspond to the Langmuir terms, k_f is the Freundlich constant related to the adsorption capacity [mg g^{-1} (mg L^{-1})^n], and n is a dimensionless empirical parameter representing the heterogeneity of the surface.

Both, Freundlich and Langmuir isotherm models, gave good correlation with the measured lignin adsorption data. Nonlinear regression was performed in order to attain the Freundlich and Langmuir coefficients (Table 5).

Figure 3 shows the Freundlich isotherms for three different adsorption temperatures (20, 150, 170 °C). Notably, the amount of lignin adsorbed per unit mass of adsorbent (q_e) significantly increased at elevated temperatures, indicating more efficient adsorption. We therefore suggest that the lignin in solution at 170 °C exhibits a different structure than at room temperature or even is in liquid state. The arrangement of hydrophilic and hydrophobic groups in this state might favour the adsorption onto activated charcoal. Validation of these assumptions will require further research in this area. Furthermore, we propose that the adsorption of lignin on AC at high temperatures follows a chemisorption process as indicated in the literature [17] and in our own preliminary desorption experiments with limited success. Elevated temperatures might provide the activation energy required for a chemisorptive process. We further suspect a change in the

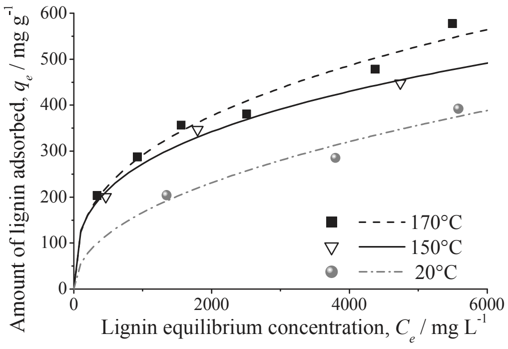

Figure 3. Freundlich isotherms (curves) and experimental adsorption data (individual points) of lignin on activated charcoal (BET surface area 880 m^2 g^{-1}) at different temperatures (20, 150 and 170 °C). q_e amount of lignin adsorbed per unit mass of AC, C_e equilibrium concentration of lignin in solution.

adsorption mechanism at temperatures beyond 100 °C, as Parajo found that in the range between 20 and 60 °C the adsorption efficiency decreased significantly with increasing temperature [19].

Due to the long adsorption times at 20 °C, it can be assumed that no significant lignin adsorption occurred during the cooling phase. Furthermore, after 80 min of adsorption at 170 °C and a charcoal amount exceeding 12 g L^{-1} no incrustations were formed (Table 4). Thus, lignin was not available for condensation reactions. This also indicates that the lignin was already adsorbed before cooling. Reference measurements without activated charcoal at the same conditions, however, yielded an amount of incrustations higher than 3.2 g L^{-1}.

Effect of activated charcoal type

Four activated charcoals with BET surface areas of 280, 560, 880 and 1270 m^{2} g^{-1} were tested for lignin adsorption. The adsorption behaviour of the different charcoals was modelled in terms of Freundlich and Langmuir isotherms, whereby the fit of the former was slightly better (mean R² of 0.94 compared to 0.92). The best adsorption results were obtained using the charcoal with the highest BET surface area (1270 m^{2} g^{-1}, Figure 4). All charcoals investigated showed small mesopore diameters (data not shown). The volume of mesopores was almost equal for the charcoals with a BET surface area of 560 and 880 m^{2} g^{-1}, but significantly higher for the charcoal of BET 1270 m^{2} g^{-1}.

The micropore volume was higher for the AC of BET 880 m^{2} g^{-1} than for 560 m^{2} g^{-1}. The micropore diameters of the AC of BET 1270 m^{2} g^{-1} were larger than for the other charcoals. The AC of BET 280 m^{2} g^{-1} exhibited only small volumes of meso- and micropores.

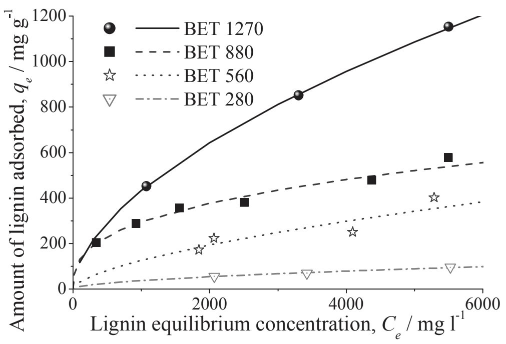

Figure 4. Freundlich isotherms (curves) and experimental adsorption data (individual points) of lignin on activated charcoals of BET surface areas of 1270, 880, 560, 260 m^{2} g^{-1} for 20 min at 170°C. q_e amount of lignin adsorbed per unit mass of AC, C_e equilibrium concentration of lignin in solution.

In terms of lignin adsorption, a decrease of the BET surface from 1270 to 880 m^{2} g^{-1} resulted in a 150 % higher demand of AC to yield a comparable lignin reduction. A further decrease of the BET surface area to 280 m^{2} g^{-1} required twelve times the amount of AC to achieve the equivalent adsorption efficiency. Taking into account the total surface area of the adsorption system as the surface area (m² g^{-1}) of the AC times the amount of AC (g L^{-1}), it can be seen that the smallest surface is needed, for the charcoal with the high volume of mesopores and larger micropores (BET 1270 m^{2} g^{-1}). A 70 % higher total surface area is needed for the charcoals with BET 560 and 880 m² g^{-1}. For the charcoal of minor microporosity (AC with BET 280 m² g^{-1}) almost three times the total surface area is needed for similar lignin removal. Thus, not only the total surface area is a criterion for lignin adsorption, but also the distribution and volume of meso- and microporosity and assumingly surface functionalities. A potential effect of the ash content and the alkalinity of the ACs on the lignin adsorption is possibly superimposed by the high differences in BET surface

Table 5. Freundlich and Langmuir coefficients calculated by nonlinear regression.

Temp. / °C	BET / m^{2} g^{-1}	Freundlich			Langmuir		
		k	1/n	R²	Q	β	R²
170	1270	8.32	0.57	1,00	1849.59	3503.8	0.98
170	880	22.83	0.37	0.97	617.70	1052.5	0.89
150	880	28.00	0.33	0.99	512.55	767.8	0.99
20	880	6.36	0.47	0.93	530.43	2456.1	0.88
170	560	1.02	0.69	0.81	884.41	7498.0	0.79
170	280	0.72	0.57	0.99	174.25	4700.1	0.97

area. The alkalinity of the AC might affect the stability of carbohydrates during the adsorption process.

Spent activated charcoal

After adsorption of lignin on an activated carbon of BET surface area 880 $m^2 g^{-1}$ at 170 °C the surface area decreases drastically to 70 $m^2 g^{-1}$. SEM images (Figure 5) show the structured surface of the activated carbon. After the adsorption process a smooth surface covered with lignin is imaged.

Table 6. BET surface after solvent desorption of lignin.

Solvent	dissolved lignin / % lignin on AC	BET / $m^2 g^{-1}$
Reference before desorption		70
NaOH (0.5 N)	10	109
Acetone/water (5/1)	21	122
Ethanol	10	95
Acetic acid	18	106
DMSO	n.d.	134

Desorption of this lignin (Table 6) using solvents yields up to 18 % of the lignin on the charcoal. However, the active surface area is not positively affected, probably due to the high binding strength of remaining lignin to the charcoal and due to the inaccessibility of lignin in the pores. This is also in agreement with the literature [28].

Conclusions

Adsorption of lignin and lignin degradation products from autohydrolysates on activated charcoals at prehydrolysis temperature is a suitable method for the prevention of scaling. The so-called HiTAC process exhibits a fairly good selectivity towards lignin adsorption without concomitant adsorption of carbohydrates up to a lignin removal of 85 % at 170 °C. At higher charcoal concentrations oligomeric sugars are increasingly adsorbed, while monomeric sugars remain unaffected. The carbohydrate dehydration products, furfural and HMF, are removed during the AC treatment to a concentration sufficiently low which allows an uninhibited fermentation of the hydrolysate. The equilibrium adsorption time is reached within a rather short period of time. Surprisingly, it could be shown that adsorption is significantly more efficient at autohydrolysis temperature (150 and 170 °C) than at room temperature, which is advantageous for purifying the hydrolysate during its discharge from the digester. The choice of an activated charcoal of high microporosity and surface area is indispensable for a successful implementation in commercial practice. It was demonstrated that the addition of activated charcoal to the hydrolysate prevents the formation of sticky precipitates efficiently. Clearly, a cost effective regeneration process for the charcoal is needed for a commercial realisation. Solvent desorption of lignin is yet not possible. Thus, it is our goal to develop an appropriate recycling strategy for the exhausted charcoal.

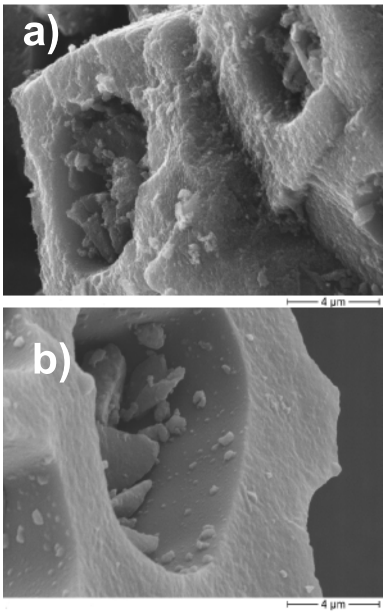

Figure 5. SEM images of activated charcoal a) before, b) after lignin adsorption.

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Paper III

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Comparative evaluation of autohydrolysis and acid-catalyzed hydrolysis of *Eucalyptus globulus* wood

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ABSTRACT

Three different acids (acetic, oxalic and sulfuric acid) were tested for their catalytic activity during the pretreatment of *Eucalyptus globulus* wood comparatively to autohydrolysis in order to extract valuable products prior to kraft pulping and to reduce lignin precipitation in the pretreatment step. The utilization of oxalic and sulfuric acid reduces treatment temperatures at a given wood yield as compared to autohydrolysis and acetic acid addition and thus decreases the insoluble lignin content in the hydrolyzates. Due to the high temperatures of autohydrolysis xylose dehydration to furfural occurs at high wood yield losses, while during acid catalyzed hydrolysis degradation of cellulose to glucose is more pronounced. The main difference between the acid catalyzed and non-catalyzed reaction constitutes the ratio of monomeric xylose and xylooligosaccharides in solution.

1. Introduction

Various process streams in pulp manufacture containing carbohydrates as a main component are currently spent as low-calorific heating material. Biorefinery concepts target the chemical utilization of those product streams and therefore provide additional economic and environmental benefit. Prehydrolyzates from the prehydrolysis kraft process are a good example for an idle process stream with high potential for the utilization as feedstock (Moure et al., 2006).

1.1. Autohydrolysis

The prehydrolysis kraft process is a well established process for dissolving pulp production (Sixta, 2006). In a first step – the autohydrolysis or hydrothermolysis – wood is treated with pure water in order to dissolve hemicelluloses that are hardly degraded in an alkaline cooking stage. During autohydrolysis the chips are impregnated easily and hydrolysis evolves uniformly, because the hydrolysis catalyst acetic acid is formed directly in the wood cells due to the cleavage of acetyl groups from the xylan backbone. The subsequent kraft cooking step removes the lignin and yields a pulp with a residual xylan content of about 3% in the case of hardwood. Sulfur-free alternatives to prehydrolysis-kraft cooking are prehydrolysis-soda-anthraquinone cooking (Schild et al., 2010) or prehydrolysis-organosolv (Romaní et al., 2011) pulping. Currently, water prehydrolysis is not implemented in industry due to the formation of highly reactive lignin precipitates that cause severe plugging problems (Leschinsky et al., 2008). To circumvent the clogging of pipes and pumps, prehydrolysis is currently carried out as steam prehydrolysis, where the hydrolyzate is neutralized and displaced to the evaporation plant prior to cooking (Wizani et al., 1994).

1.2. Acid catalyzed prehydrolysis

Acid prehydrolysis is applied to remove hemicelluloses for (dissolving) pulp production (Liu et al., 2009). It is seen as a novel source of chemicals, either via total hydrolysis of lignocellulosic biomass to sugar monomers or as a pretreatment of biomass for enzymatic conversion (Grethlein and Converse, 1991). In mechanical pulping acid prehydrolysis is applied in order to soften the wood structure and therefore save refining energy (Kenealy et al., 2007). In the biorefinery approach these different strategies and aims are combined to yield the most efficient utilization of all wood components (Yoon et al., 2008). The pretreatment of biomass with sulfuric acid is rather traditional and therefore most intensely studied on a wide range of substrates including wood and annual plants (Jeong et al., 2010; Parajó et al., 1994; Springer, 1985). Nevertheless other inorganic acids like hydrochloric acid (Conner,

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1985) and recently organic acids like acetic acid (Conner and Lorenz, 1986), maleic acid and oxalic acid (Kenealy et al., 2007; Lee and Jeffries, 2011; Rudie et al., 2007) were investigated regarding their ability to liberate monomeric sugars. As a consequence of acid addition, prehydrolysis intensities and therefore treatment costs are reduced. Current pulping developments aim to avoid the addition of environmentally unfavorable heteroatoms like sulfur or chloride in the pulping system, therefore organic acids offer the possibility of a sulfur free pretreatment that is less corrosive. In any case, the utilization of acids causes additional costs, therefore recirculation possibilities must be kept in mind.

1.3. Chemical composition of the hydrolyzates

1.3.1. Lignin

Wood lignin partly dissolves at prehydrolysis conditions and precipitates upon cooling, which can be hardly avoided (Leschinsky et al., 2008). However, shorter prehydrolysis times and lower temperatures, accomplished via acid catalysis, reduce the amount of lignin in the hydrolyzate. A high lignin content in the hydrolyzate causes major difficulties in the recovery of carbohydrate components because of precipitation and formation of incrustations.

Up to now a drastic decrease of precipitated lignin was only observed when SO_2 was added. Due to sulfonation the overall solubility of lignin, however, increased significantly, yielding high amounts of soluble lignosulfonates in the prehydrolyzates, thus counteracting to the intended selectivity (Leschinsky, 2009). Tunc and van Heiningen (2011) used centrifugation for the removal of lignin precipitates, but still found lignin in all hemicellulosic fractions recovered. In the course of membrane filtration lignin causes serious fouling of the membranes and renders this process impossible without additional pretreatment (Gullon et al., 2008; Kallioinen et al., 2011). Thus, the removal of lignin from the prehydrolyzates immediately after hydrolysis is necessary. This is realized within the HiTAC-process (high temperature adsorption on activated charcoal), where lignin is selectively adsorbed on activated charcoal at prehydrolysis temperature (Gütsch and Sixta, 2011).

1.3.2. Carbohydrates

The main component dissolved during acid prehydrolysis of hardwoods is xylan, either dissolved as monomeric xylose or as xylooligomers (XOS). Autohydrolysis liberates hemicelluloses in oligomeric form which are degraded to less substituted oligosaccharides of lower molar mass and further to monomeric sugars with increasing treatment intensity (Testova et al., 2011). This consecutive reaction is considerably accelerated during sulfuric acid catalyzed hydrolysis. With increasing hydrolysis intensity parts of the amorphous cellulose start to hydrolyze, increasing the concentration of cello-oligosaccharides and glucose in the hydrolyzate (Borrega et al., 2011). Before C_6-sugars are enriched in the hydrolyzates, cellulose depolymerization occurs, which in turn leads to significant yield losses in subsequent alkaline pulping operations owing to peeling reactions (BeMiller, 1967).

Maleic, oxalic and sulfuric acid showed considerable differences in the carbohydrates released to the hydrolyzates. Maleic acid yielded higher amounts of xylose, but was less selective towards glucose at the same severity factor. Contrary to maleic acid, oxalic and sulfuric acid hydrolysis at low severities led to a small fraction of oligomers (Lee and Jeffries, 2011).

The aim of this study was to comparatively evaluate the influence of water autohydrolysis and acid-catalyzed hydrolysis of *Eucalyptus globulus* wood chips with reference to their potential of providing a substrate for xylan-derived products. Acetic acid, oxalic acid and the mineral acid sulfuric acid were used as acid catalysts. Acetic acid was chosen for direct comparison to autohydrolysis, because it is the actual catalyst within the autohydrolytic treatment. Sulfuric acid is a classical hydrolysis catalyst. In order to avoid sulfur in the system – for ecological reasons – the strong dicarboxylic acid oxalic acid was chosen in comparison to sulfuric acid. Special attention was paid to the influence of acid catalysts towards the dissolution and precipitation behavior of lignin in the hydrolyzates.

2. Methods

2.1. Wood chips

E. globulus wood chips from plantations in Uruguay were supplied by ENCE (Huelva, Spain). The chips were ground with a Retsch-type grinding mill and fractionated. The fraction with particle sizes between 2.5 and 3.5 mm was collected and used for the prehydrolysis experiments. The dry content of the wood chips (82.9%) was measured after drying at 104 °C until constant weight (48 h). The carbohydrate content of wood chips (39.9% glucan, 14.9% xylan, 0.1% rhamnan, 0.3% arabinan, 0.4% mannan and 1.3% galactan) was analyzed after a two-stage total hydrolysis by high performance anion exchange chromatography with pulsed amperometric detection (Sixta et al., 2001). Klason lignin (23.6%) and acid soluble lignin (4.8%) were measured according to Tappi T222om 98, ash content (0.32%) according to DIN 54370 at 850 °C.

2.2. Prehydrolysis

Prehydrolysis was carried out in a lab-scale Parr reactor station with a reactor volume of 450 ml, mechanical stirring and temperature control. Fifty grams of wood were placed inside the reactor. Deionized water was added to achieve a liquor-to-wood ratio of 5:1. For acid catalysis sulfuric acid (0.01–0.1 M), oxalic acid (0.01–0.1 M) and acetic acid (0.02–0.15 M) were added, respectively. The reactor was heated up to prehydrolysis temperature (120–200 °C) within minimum heating time (approximately 30 min), the temperature was maintained for the prehydrolysis time (10–120 min). The prehydrolyzate was subsequently separated from the wood residue by displacement with nitrogen to a preheated second reactor containing saturated steam with a temperature of 170 °C following the protocol of Leschinsky (2009).

Both reactors were immediately cooled to below 30 °C with ice water after the phase separation step. Contained within the cold crude autohydrolyzate was an insoluble fraction, causing turbidity. This insoluble fraction (I) was separated from the soluble part of the hydrolyzate (S) by centrifugation for 15 min at 4500 rpm. The wood residue was then washed with 2 l of 70 °C deionized water. S-fraction, I-fraction and the washed wood residue (WR) were quantitatively collected and analyzed.

2.3. Intensity of prehydrolysis

The intensity of autohydrolysis of *E. globulus* wood chips is conveniently expressed as *p*-factor using an Arrhenius-type expression. A value of 125.6 kJ mol^{-1} for the fast-reacting xylan (X_F), based on extensive investigations of xylan hydrolysis from *E. saligna*, has been suggested for the *p*-factor (P_{X_F}) calculation in a prehydrolysis kraft pulp mill (Sixta, 2006):

$$P_{X_F} = \int_{t_0}^{t} \exp\left(40.48 - \frac{15106}{T}\right) dt \qquad (1)$$

where t is the residence time in minutes and T the reaction temperature measured in °C. Overend and Chornet introduced the severity factor R_0 to quantify the intensity of hydrothermal biomass treatment using the following expression (Overend and Chornet, 1987):

$$R_0 = t \exp\left(\frac{T - 100}{14.75}\right) \tag{2}$$

where t is the residence time in minutes and T the reaction temperature measured in °C. The logarithmic plot of R_0 allows the illustration of the data in a more condensed form. To account for the addition of catalysts such as sulfuric acid and oxalic acid in Eq. (2) the initial proton concentration in the pre-treatment was considered according to Eq. (3) (Abatzoglou et al., 1992):

$$R_0' = R_0 \cdot [\mathrm{H}^+] = \log(R_0) - \mathrm{pH} \tag{3}$$

2.4. Analytical methods

The total carbohydrate composition of S, WR, and the original wood were investigated using high performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD) after two-stage sulfuric acid total hydrolysis (TH) (Sixta et al., 2001). Carbohydrate monomers in the S-fraction were analyzed without TH. Furfural and hydroxymethylfurfural (HMF), which are formed during TH from pentoses and hexoses, were quantified and added to the results for xylose and glucose, respectively. Determinations by TH/HPAEC-PAD were performed at least thrice and twice, respectively. The amount of sugar oligomers contained in S was calculated by subtracting the monomer content from the results determined after TH.

Furfural and hydroxymethylfurfural (HMF) in S and in the acid hydrolyzates were measured by HPLC on a Hypersil ODS column with UV detection (277 nm) using 14% (v/v) acetonitrile as eluent at a temperature of 65 °C.

Acetic acid in S was determined by HPLC on a Rezex ROA column with RI detection using 0.005 M H_2SO_4 as eluent at a temperature of 65 °C. The acetyl groups in S, WR and in the native wood were determined as acetic acid measured by HPLC subsequent to TH.

Klason lignin (KL) and acid soluble lignin (ASL) were determined according to TAPPI T222om 98 and TAPPI UM 250, respectively, in the original wood and in the WR. The WR was not extracted prior to the Klason determination due to the increased solubility of lignin in organic solvents after prehydrolysis. The lignin concentration in S was estimated similar to that of ASL from the UV/Vis spectra, which was recorded using an absorption coefficient of 110 $\mathrm{l\,(g\,cm)^{-1}}$ at 205 nm according to Tappi 1991 um 250.

3. Results and discussion

3.1. Intensity of prehydrolysis

Wood yield in autohydrolysis treatment decreases sharply with increasing treatment intensity. Autohydrolysis of *p*-factors higher than 1500 yield a constant wood yield of 65% (Fig. 1a). Acetic acid prehydrolysis generally follows the trends of autohydrolysis. Although a dependency from acid concentration is clearly visible in acetic acid pretreatment, the additional amount of acetic acid does not promote autohydrolysis sufficiently to fit the model of Abatzoglou et al. (1992), who considered the initial proton concentration to account for the addition of catalysts. The wood yields of the inorganic sulfuric acid and the organic oxalic acid pretreatments of *E. globulus* at different temperature–time–acid strength combinations are both properly described by the model of Abatzoglou using the initial proton concentration.

Fig. 1b shows the slightly sigmoidal curve of wood yield of sulfuric and oxalic acid logarithmically plotted versus R_0'. Thus, the wood yield can be adequately predicted by the R_0' value. In the following, the wood yield will be used as the main parameter to allow a better comparability of all treatments (autohydrolytic and acid catalyzed).

3.2. Lignin mass balance

Autohydrolysis is known as a rather selective method for the removal of hemicelluloses from the wood matrix. Nevertheless a significant amount of lignin is colloidally dissolved during autohydrolysis leading to precipitations after cooling and serious scaling problems during further processing of the hydrolyzates. In a previous paper (Gütsch and Sixta, 2011) we already described a method for the removal of lignin from the hydrolyzates using activated charcoal adsorption at high temperatures – the so called HiTAC-process (high temperature adsorption on activated charcoal). Still, it would be favorable to possess a pretreatment process where the overall lignin dissolution and precipitation is small, in order to save costs during downstream-processing of the hydrolyzates. The utilization of acid catalysts was thought to decrease the temperature and therefore lignin condensation and precipitation. In order to obtain full information of the process all lignin fractions (Klason lignin and acid soluble lignin of the residual wood, soluble and insoluble lignin in the hydrolyzate) were quantified (Tables 1–3). Klason lignin (KL) in wood does not decrease with increasing treatment intensity. KL content of the catalytically hydrolyzed wood samples is in the range of the original wood (24%) and is independent from process conditions (Fig. 2). Acid strength and type of acid do not alter KL content of the hydrolyzed wood at a comparable wood yield level. However, during autohydrolysis a slightly reduced Klason lignin content was observed, although scattering of the results leaves some insecurity. It is therefore assumed that KL is not the source of dissolved lignin in the acid hydrolyzates, but might be of some importance during autohydrolysis. In either case KL after prehydrolysis is known to be structurally changed, as it is more easily extracted with organic solvents (Leschinsky, 2009; Lora and Wayman, 1980) and with alkali (Lora and Wayman, 1978). Thus no extraction step was applied prior to KL determination.

With increasing wood loss the amount of acid soluble lignin (ASL) is reduced from 4.8% odw to below 1% odw in both autohydrolysis and acid catalyzed hydrolysis experiments to a similar extent. Thus, ASL is the main lignin moiety dissolved in the slightly acidic aqueous hydrolyzates. The values of ASL after oxalic acid catalyzed hydrolysis show a higher deviation from a linear relation, but are in general in the range of those of the other pretreatment methods.

In the hydrolyzates two lignin fractions were collected according to Leschinsky et al. (2009): soluble (S) lignin (Fig. 3b) and insoluble (I) precipitated lignin (Fig. 3a) that was separated from the soluble fraction via centrifugation. S-lignin in the hydrolyzate increases with decreasing wood yield to the same extent than ASL in the wood residue decreases. The amount of I-lignin does not follow a distinct trend in respect to wood yield, but especially at increased wood yield losses, autohydrolysis and acetic acid hydrolysis show a considerably higher amount of I-fraction as compared to sulfuric and oxalic acid pretreatments. Thus, ASL is responsible for both I- and S-lignin in sulfuric and oxalic acid hydrolysis, during autohydrolysis the loss in KL adds up to an increased value of I-fraction lignin. The formation of an I-fraction during autohydrolysis is extremely temperature dependent. Experiments performed at 150 °C lead to significantly less I-lignin than experiments performed at 170 °C at similar wood yield levels (Fig. 3a). The same trend was visible for acetic acid experiments. The drastic decrease of I-lignin in autohydrolyzates at a process temperature of 200 °C (wood yields of 63–68%) is a consequence of two effects: First, isothermal displacement of the hydrolyzate was not possible at the high water vapor pressure at 200 °C. Therefore reprecipitation of lignin on the wood chips is assumed,

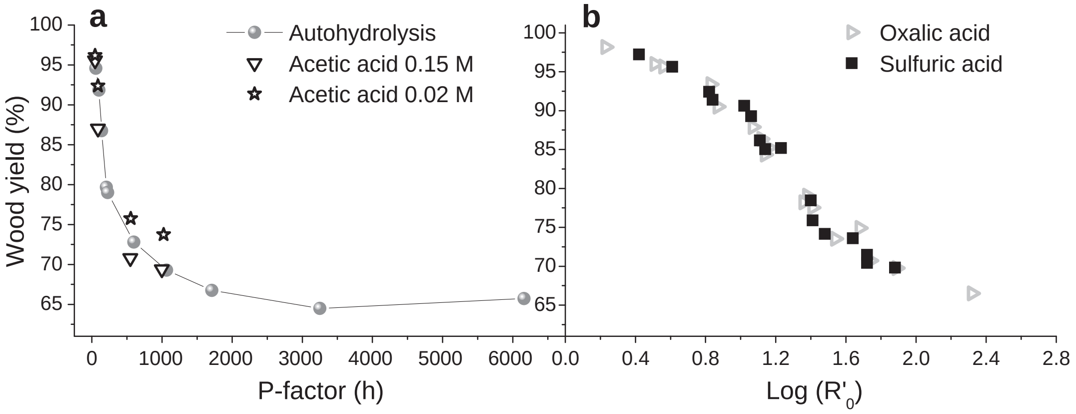

Fig. 1. Wood yields of (a) autohydrolysis and acetic acid pretreatment as a function of *p*-factor and (b) sulfuric acid and oxalic acid prehydrolysis as a function of R'_0.

Table 1
Composition of the hydrolyzates and the residual wood after oxalic acid catalyzed hydrolysis.

Acid	Oxalic acid												
Process conditions													
Acid concentration (mol l^{-1})	0.01			0.02		0.05		0.10					
Temperature (°C)	120	120	140	120	140	120	120	120	140	140	140	140	160
Time (min)	51	97	57	61	56	55	97	72	30	45	71	100	69
Wood yield (%)	98.2	96.0	90.5	95.7	86.4	93.4	87.9	85.2	78.2	73.5	70.7	69.8	66.5
Composition of hydrolyzates (% odw)													
Monomeric glucose	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.2	0.4	0.7	0.8	1.1	2.4
Monomeric xylose	0.0	0.0	0.3	0.1	2.1	0.6	2.1	4.3	8.5	11.9	13.3	13.5	11.9
Other sugar monomers	0.2	0.4	0.6	0.5	1.1	0.8	1.1	1.3	1.7	2.1	2.4	2.3	2.3
Oligomeric glucose	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.3
Oligomeric xylose	0.1	0.2	1.8	0.4	3.0	1.0	1.8	1.5	0.3	0.0	0.0	0.0	1.2
Other sugar oligomers	0.3	0.3	0.4	0.3	0.5	0.3	0.3	0.2	0.1	0.0	0.1	0.0	0.1
Furfural	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.4	0.6	1.5
HMF	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Free acetic acid	0.0	0.1	0.3	0.2	0.8	0.5	1.1			0.1	3.5	0.3	3.7
I-fraction lignin	0.2	0.2	0.4	0.2	0.6	0.3	0.2	1.7	3.1		1.1	0.9	0.3
S-fraction lignin	1.4	1.5	2.0	1.5	2.5	1.7	2.0	2.5	2.9	3.2	3.2	3.4	5.4
Sum of compounds in hydrolyzate	2.4	3.0	6.2	3.5	11.0	5.3	9.0	11.6	17.1	18.4	24.9	22.2	29.1
Composition of residual wood (% odw)													
Glucan	39.3	39.7	39.3	39.8	40.0	40.0	39.5	41.7	40.5	42.1	37.8	41.3	36.7
Xylan	13.5	13.2	10.4	12.7	7.8	11.6	9.8	8.6	5.4	3.0	2.6	1.8	0.9
Other carbohydrates in wood	2.3	2.0	1.5	2.0	1.2	1.7	1.2	1.0	0.7	0.4	0.5	0.3	0.2
KL	24.6	24.2	24.2	24.5	24.5	24.1	23.6	23.01	22.59	23.4	21.2	23.3	23.6
ASL	4.5	4.1	3.1	4.8	2.6	4.9	4.0	3.28	2.55	1.6	1.4	1.3	1.2
Sum of compounds in wood residue	84.1	83.2	78.6	83.7	76.2	82.4	78.1	77.6	71.7	70.6	63.5	68.0	62.6

which is supported by an increase in the KL content in the wood residue of two samples (Fig. 2). Second, a large fraction of incrustations was formed on the equipment at 200 °C, which was not possible to quantify, but is reported to consist of lignin mainly (Leschinsky, 2009). The immediate formation of incrustations was only monitored for the 200 °C autohydrolysis experiments.

3.3. Distribution of xylan

The main goal of an acidic pretreatment prior to kraft cooking is the solubilization of xylan in order to yield a pulp of high cellulose purity and to obtain a hydrolyzate for the production of valuable xylan based products. The xylan content of the wood residue decreases linearly with decreasing wood yield for all treatments investigated (Fig. 4a). Xylan can be almost completely removed from the wood matrix even by using pure water autohydrolysis at high prehydrolysis intensities. The high intensities applied for complete xylan removal (200 °C, 70 min isothermal time), however, lead to extensive xylan hydrolysis and decarboxylation (Leschinsky et al., 2009) and increasing amounts of furfural are formed from xylose through dehydration reactions (Fig. 5a). The utilization of inorganic and organic acids allows running prehydrolysis at lower temperatures and reaction times which in turn contributes to lower energy consumption. The addition of 0.1 M sulfuric acid reduces temperature and treatment time needed for a residual xylan content of 2% odw from 170 °C and 100 min to 140 °C and 35 min as compared to autohydrolysis (Tables 2 and 3).

Oxalic acid, a strong dicarboxylic organic acid, is considered to have a high potential for biomass pretreatment since xylan is selectively dissolved and no evidence of cellulose degradation was found in literature (Kenealy et al., 2007). Prehydrolysis using oxalic acid as catalyst results in a lower amount of residual xylan at a given wood yield than was observed for the other treatments investigated (Fig. 4a). This is indicative for a better selectivity of the oxalic acid pretreatment. However, this surplus of dissolved xylan was not recovered in the hydrolyzate, where the total xylose content equals those of sulfuric acid catalysis. Oxalic acid is increasingly consumed with progressing prehydrolysis. At a wood yield of 66% an oxalic acid loss of 78% was observed in the hydrolyzates (data not shown).

The complete compositional analyses of both the liquid and solid phases are shown for oxalic acid, sulfuric acid catalyzed

Table 2
Composition of the hydrolyzates and the residual wood after sulfuric acid catalyzed hydrolysis.

Acid	H_2SO_4											
Process conditions												
Acid concentration (mol l^{-1})	0.01				0.05				0.10			
Temperature (°C)	120	120	140	140	120	120	140	140	120	120	140	140
Time (min)	68	104	69	44	36	67	40	70	36	65	35	50
Wood yield (%)	97.2	95.6	90.6	92.4	91.4	86.2	74.2	71.5	85.1	78.5	70.4	69.8
Composition of hydrolyzates (% odw)												
Monomeric glucose	0.0	0.0	0.0	0.0	0.1	0.2	0.5	0.8	0.2	0.4	0.9	1.0
Monomeric xylose	0.0	0.2	0.3	0.0	1.0	3.3	10.3	12.2	4.6	8.6	13.1	12.6
Other sugar monomers	0.0	0.6	0.6	0.4	0.8	1.2	2.1	2.4	1.4	1.8	2.4	2.3
Oligomeric glucose	0.2	0.3	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.1
Oligomeric xylose	0.1	1.6	1.3	0.4	1.3	2.0	0.4	0.0	1.2	0.3	0.0	0.0
Other sugar oligomers	0.5	0.6	0.5	0.5	0.3	0.3	0.1	0.1	0.2	0.1	0.0	0.1
Furfural	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.4	0.0	0.1	0.4	0.7
HMF	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Free acetic acid	0.1	0.2	0.3	0.2	0.8	1.2	2.1	n.d.	1.9	2.6	3.5	3.5
I-fraction lignin	0.1	0.2	0.5	0.6	0.3	0.3	0.6	0.6	0.1	0.2	0.7	0.7
S-fraction lignin	1.2	1.9	2.1	1.4	1.9	2.3	3.1	4.2	2.1	2.9	3.8	3.4
Sum of compounds in hydrolyzate	2.2	5.6	6.0	3.8	6.7	11.1	19.5	20.7	11.9	17.0	25.0	24.4
Composition of residual wood (% odw)												
Glucan	39.1	39.4	40.0	39.9	39.0	39.8	39.3	40.6	47.4	39.3	38.3	38.7
Xylan	13.8	13.6	11.4	12.6	11.5	9.0	3.5	2.4	2.1	5.3	2.0	1.7
Sum of other carbohydrates in wood	2.0	2.1	1.4	1.7	1.4	1.2	0.5	0.4	0.3	0.9	0.3	0.2
KL	24.7	24.2	24.6	24.4	24.2	24.3	23.6	24.3	25.4	23.7	20.1	23.7
ASL	3.9	3.6	3.0	3.4	4.0	3.2	1.7	1.5	4.0	4.0	1.3	3.0
Sum of compounds in wood residue	83.5	83.0	80.3	82.0	80.0	77.5	68.6	69.1	79.2	73.1	62.1	67.2

Table 3
Composition of the hydrolyzates and the residual wood after autohydrolysis.

Process conditions										
Temperature (°C)	150				170			200		
Time (min)	29	50	69	113	7	18	60	20	37	70
Wood yield (%)	94.58	91.85	86.76	79.01	91.95	83.19	72.80	66.76	64.49	65.73
Composition of hydrolyzates (% odw)										
Monomeric glucose	0.0	0.0	0.0	0.1	0.0	0.1	0.2	0.3	0.6	0.8
Monomeric xylose	0.0	0.1	0.1	0.6	0.0	0.3	3.8	4.8	2.1	0.2
Other sugar monomers	0.2	0.3	0.4	0.8	0.2	0.7	1.3	1.1	0.8	0.2
Oligomeric glucose	0.2	0.3	0.3	0.3	0.2	0.3	0.4	0.5	0.5	0.4
Oligomeric xylose	0.5	1.5	3.2	7.4	0.6	5.5	7.7	7.0	6.5	5.1
Other sugar oligomers	0.5	0.7	0.9	0.9	0.4	0.7	0.9	0.6	0.1	0.1
Furfural	0.1	0.0	0.0	0.1	0.0	0.1	0.7	2.0	3.9	4.3
HMF	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.4	0.7
Free acetic acid	0.1	0.2	0.3	0.7	0.22	1.44	n.d.	3.7	4.8	4.6
I-fraction lignin	0.8	0.8	0.4	1.1	1.4	1.6	1.7	1.3	0.2	0.2
S-fraction lignin	1.8	2.3	2.8	3.3	2.0	3.0	3.3	4.2	4.3	4.3
Sum of compounds in hydrolyzate	4.3	6.2	8.5	15.3	4.8	12.2	20.1	25.5	24.2	20.9
Composition of residual wood (% odw)										
Glucan	40.3	40.0	38.9	38.8	42.3	42.4	37.3	39.0	36.1	37.8
Xylan	13.9	12.6	10.7	6.8	13.7	8.4	3.9	1.6	0.8	0.5
Other carbohydrates in wood	2.1	1.8	1.6	1.0	1.5	1.0	0.7	0.1	0.0	0.0
KL	23.1	23.0	23.0	23.4	22.3	22.5	23.0	21.5	22.5	24.5
ASL	3.8	3.4	2.9	1.9	3.8	2.8	1.5	0.9	0.7	0.8
Sum of compounds in wood residue	83.0	80.8	77.2	71.9	83.6	77.1	66.4	63.1	60.2	63.5

hydrolysis and autohydrolysis of *E. globulus* in Tables 1–3, respectively. During sulfuric acid and oxalic acid catalyzed hydrolysis almost all sugars dissolve as monomeric sugars immediately (Fig. 4b and c), only at rather mild process conditions up to 2% odw oligomeric xylan is detected in the hydrolyzate. At more severe process conditions (wood yield < 85%, $\log R_0' > 1$), however, no oligomers are found in sulfuric and oxalic acid catalyzed hydrolyzates. The amount of monomeric xylose in the sulfuric and oxalic acid hydrolyzates increases linearly with a proceeding hydrolysis depth until almost all xylan of wood is dissolved as monomers. Thus, the isolation of XOS using dilute sulfuric and oxalic acid hydrolysis is not possible. However, the utilization of monosugars for biofuel production has been a great research focus in the last years (Marinova et al., 2010). After neutralization of the acids and the removal of inhibitors sulfuric and oxalic acid prehydrolyzates are a possible feedstock for the production bioethanol and other monosugar derived products.

Autohydrolysis and acetic acid-catalyzed hydrolysis of *E. globulus* reveal a similar reaction pattern reflected in the comparable composition of both the wood residues and the hydrolyzates (Tables 3 and 4). During autohydrolysis and acetic acid hydrolysis xylan is solubilized in oligomeric or low polymeric form. Oligomeric xylan concentration in autohydrolyzates exhibits a maximum at wood yields of 70–75%. As shown in Fig. 4c, monomeric xylose in the hydrolyzate appears only at intensities representing a wood yield lower than 80%. Maximum concentrations of monomeric

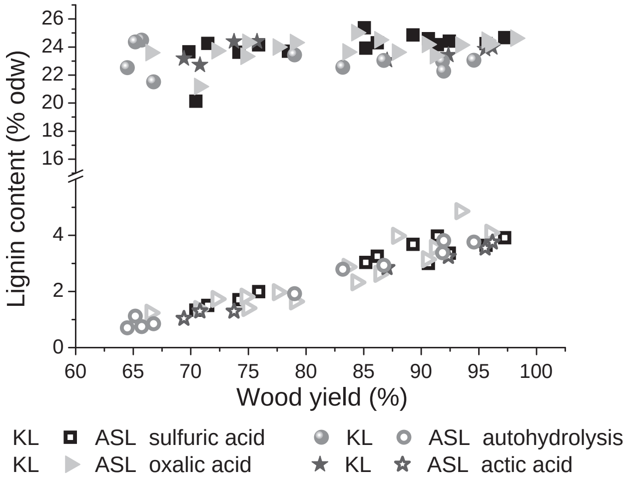

Fig. 2. Klason lignin (KL) and acid soluble lignin (ASL) of the wood residues of sulfuric, oxalic and acetic acid pretreatment and autohydrolysis.

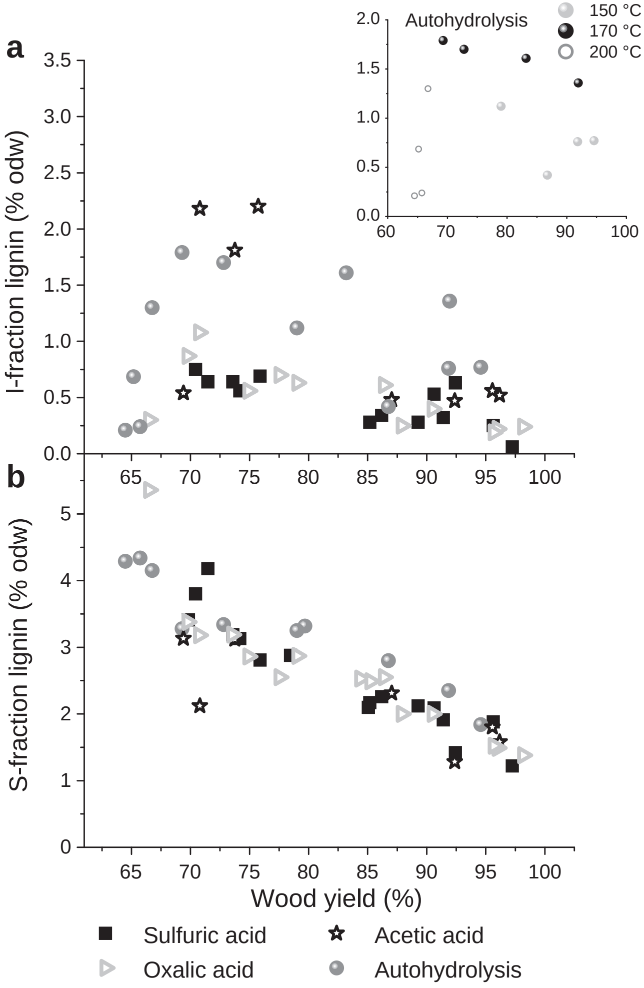

Fig. 3. (a) Insoluble (I) and (b) soluble (S) lignin in the hydrolyzates as a function of wood yield.

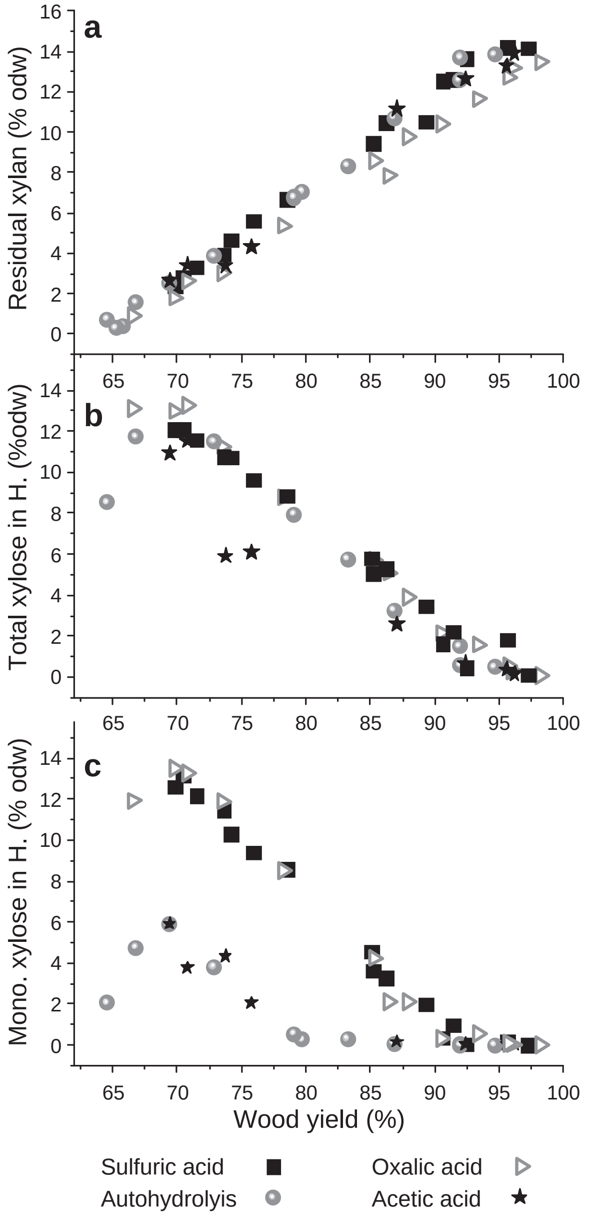

Fig. 4. Xylan distribution: (a) residual xylan in wood residue, (b) total xylose in hydrolyzate (H) and (c) the fraction of monomeric xylose thereof.

xylose (6% odw) are present at intensities corresponding to a wood yield of 70%. Higher intensities favor consecutive reactions, such as the dehydration of xylose to furfural (Fig. 5a). Due to the high amounts of oligomeric xylose autohydrolyzate is a promising feedstock for the production of xylooligosaccharides (XOS) based products, provided that suitable separation technologies are available. The polymeric xylan fraction may be separated by means of solvent precipitation. However, the economic feasibility is doubtful since only very low amounts of polymeric xylan with reasonable molar mass can be recovered from autohydrolyzates (Tunc and van Heiningen, 2011).

3.4. Xylan dehydration and deacetylation

Dehydration of xylose to furfural is negligible in all pretreatments investigated at a wood yield of 75–100% (Fig. 5a). At higher wood yield losses the formation of furfural increases steadily. This effect is most pronounced during autohydrolysis and acetic acid hydrolysis due to the higher temperatures of 170 and 200 °C applied that favor the formation of furfural up to a concentration of 4% odw. The low temperature and short treatment time of sulfuric acid catalyzed hydrolysis suppresses the formation of furfural to maximum amounts of 0.7% odw. Acid catalyzed hydrolysis does

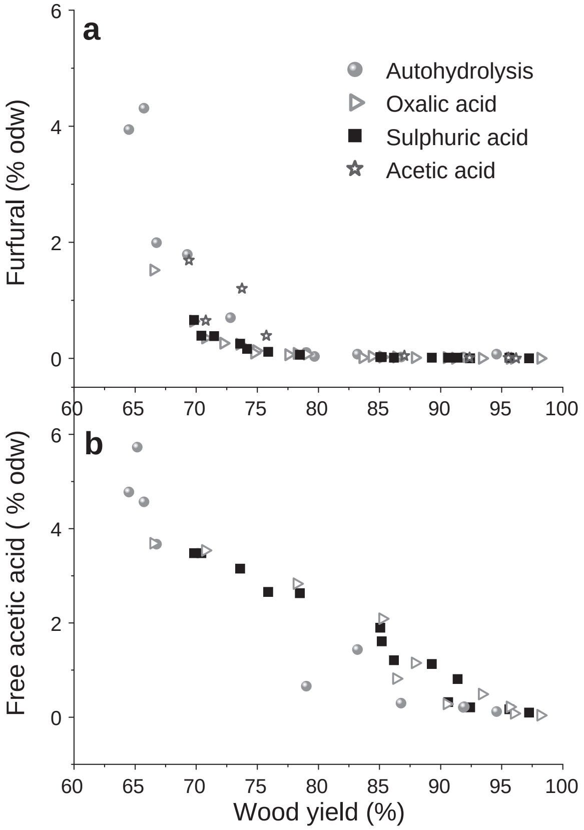

Fig. 5. Formation of (a) furfural and (b) free acetic acid during prehydrolysis as a function of wood yield.

not immediately result in reasonably high furfural yields under the conditions appropriate for dissolving pulp manufacture, the released monomeric xylose in the hydrolyzate could, however, be efficiently converted to furfural in a subsequent acid catalyzed dehydration step.

During autohydrolysis acetyl groups are hydrolytically cleaved from the xylan backbone and the acetic acid released acts as a catalyst for hydrolysis (Garrote et al., 2002). The amount of free acetic acid increases drastically at high autohydrolysis intensities, but is generally lower for autohydrolysis than for acid catalyzed hydrolysis at a higher wood yield. The cleavage of acetyl groups in sulfuric and oxalic acid hydrolysis follows a linear trend with regard to the wood yield (Fig. 5b). Beside its function as a catalyst during autohydrolysis, acetic acid might be interesting as a side product of prehydrolysis. Further, it could be used to promote hydrolysis of carbohydrates from wood. Thus, experiments were carried out using acetic acid as an additional catalyst. The amounts of acetic acid (3.6% and 0.6% odw) were chosen in order to be comparable to the amounts of acetic acid in autohydrolysis of a high and a low intensity level, respectively. Despite the additional amount of acetic acid in the process, the composition of the hydrolyzates and the wood residues remained basically unchanged in comparison to those resulting from autohydrolysis. Thus, it can be concluded that the acidity created by the addition of acetic acid, even in high amounts, is too low to accelerate the hydrolytic cleavage of carbohydrates relative to the pure autohydrolysis process (see Section 3.2.).

3.5. Cellulose hydrolysis

Wood cellulose is rather stable towards acidic degradation (Sjöström, 1981). Nevertheless, cellulose depolymerizes with progressive prehydrolysis which in turn promotes increasing yield losses in subsequent alkaline cooking owing to the formation of new reducing end groups (Sixta, 2006). Maximum glucan losses in the *E. globulus* wood residue at the highest intensities applied (wood yield < 67%) correspond to less than 2% odw. The amount of glucose in the hydrolyzates is almost negligible up to a wood yield of 80% (Fig. 6a). Exceeding this intensity mainly monomeric glucose dissolves in the hydrolyzate, during autohydrolysis as well as during acid catalyzed hydrolysis. During sulfuric and oxalic acid treatment, however, glucose dissolves more readily with a steeper slope than during acetic acid treatment and autohydrolysis. It is therefore expected, that chain scission within the WR also takes

Table 4
Composition of the hydrolyzates and the residual wood after acetic acid catalyzed prehydrolysis.

Acid	Acetic acid							
Process conditions								
Acid concentration (mol l^{-1})	0.020				0.150			
Temperature (°C)	140	140	170	170	140	140	170	170
Time (min)	55	103	56	103	55	105	55	100
Wood yield (%)	96.18	92.37	75.74	73.75	95.56	87.04	70.79	69.41
Composition of hydrolyzates (% odw)								
Monomeric glucose	0.0	0.0	0.1	0.2	0.0	0.0	0.2	0.3
Monomeric xylose	0.0	0.1	2.1	4.3	0.0	0.2	3.8	5.9
Other sugar monomers	0.1	0.3	1.1	1.2	0.3	0.5	1.3	1.4
Oligomeric glucose	0.2	0.2	0.3	0.2	0.2	0.3	0.3	0.3
Oligomeric xylose	0.1	0.6	4.0	1.6	0.3	2.4	7.7	5.0
Other sugar oligomers	0.4	0.6	0.5	0.3	0.4	0.7	0.8	0.5
Furfural	0.0	0.0	0.4	1.2	0.0	0.0	0.7	1.7
HMF	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.2
Free acetic acid	0.6	0.8	1.7	2.6	3.6	4.5	5.4	3.7
I-fraction lignin	0.5	0.5	2.2	1.8	0.6	0.5	2.2	0.5
S-fraction lignin	1.6	1.3	3.3	3.1	1.8	2.3	2.1	3.1
Sum of compounds in hydrolyzate	3.6	4.3	15.8	16.7	7.3	11.5	24.4	22.6
Composition of residual wood (% odw)								
Glucan	40.4	39.5	39.2	39.3	39.0	38.3	38.6	37.6
Xylan	13.9	12.6	4.3	3.4	13.3	11.2	3.4	2.6
Other carbohydrates in wood	2.0	1.8	0.7	0.6	2.0	1.6	0.6	0.5
KL	24.0	23.4	24.4	24.4	23.8	23.1	22.7	23.2
ASL	3.8	3.2	1.6	1.3	3.5	2.8	1.3	1.0
Sum of compounds in wood residue	84.0	80.6	70.2	68.9	81.7	76.9	66.6	64.9

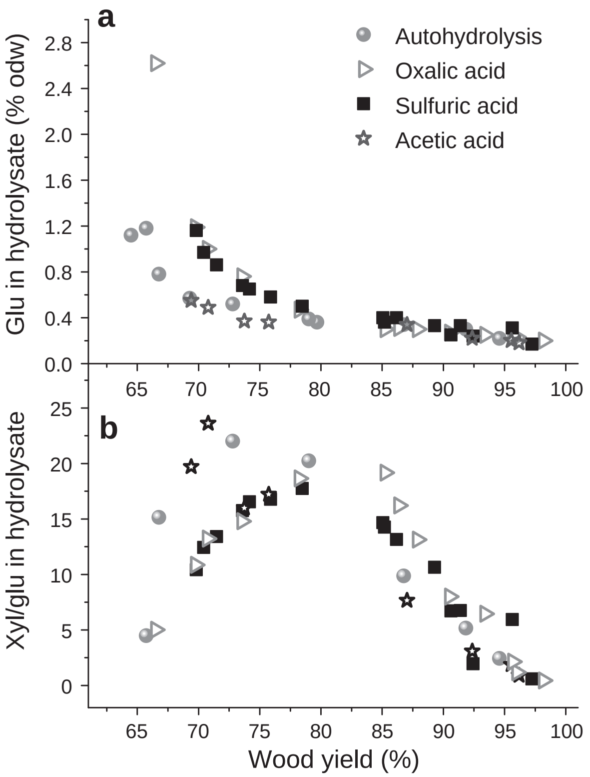

Fig. 6. (a) Losses due to solubilized glucose in the hydrolyzates and (b) selectivity of the hydrolysis reactions given as the ratio of xylose to glucose in hydrolyzate.

place to a higher extent. Thus, pulp yield and viscosity after cooking are expected to be lower using acid catalyzed hydrolysis as compared to autohydrolysis as a pretreatment step.

The increasing degradation of glucose leads to an operational optimum, where the ratio of xylose to glucose in solution is maximal (Fig. 6b). For sulfuric and oxalic acid hydrolysis of *E. globulus* this optimum is maintained at a wood yield of about 80%. For acetic acid hydrolysis and autohydrolysis a higher xylose-to-glucose ratio is attained at wood yields of 70% which is explained mainly by the slower glucose solubilization.

4. Conclusions

Autohydrolysis of *E. globulus* dissolves xylooligomers and monomers, while the addition of sulfuric and oxalic acid favors the immediate dissolution of monomeric xylose. At a given wood yield similar amounts of xylan are extracted. Oxalic and sulfuric acid react similarly on the dissolution of wood and the hydrolyzate composition. At wood yields below 80% glucose dissolution is enhanced using acid catalysts, thus reduced yields are expected during subsequent kraft cooking. Lignin in the hydrolyzate originates from acid-soluble lignin in wood. The amount of insoluble lignin is drastically reduced using strong acid catalysts, simplifying downstream processing. The surplus of insoluble lignin in autohydrolyzates derives from Klason lignin in wood.

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Paper IV

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Regeneration of Spent Activated Charcoals Used for Lignin Removal from Prehydrolysis-Kraft Prehydrolyzates

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ABSTRACT: Lignin in prehydrolysis-kraft prehydrolyzates leads to incrustations and impedes the utilization of the hemicellulosic fraction as a product. The adsorption of the lignin on activated charcoal directly after prehydrolysis at prehydrolysis temperatures prevents the formation of these incrustations efficiently. However, reutilization of the charcoal is necessary to ensure an economic process. To develop adequate recycling strategies for the spent activated charcoal, solvent extraction and thermal regeneration were investigated with respect to the recycling performance of the regenerated charcoals. Solvent extraction of the spent charcoals showed only limited efficiency, while the adsorption capacity of the activated charcoal was quantitatively restored by a thermal treatment at 950 °C. This was demonstrated by a pore size distribution and a lignin adsorption behavior of the recycled activated charcoal comparable to that of a fresh one which allows the reutilization of the charcoal in the adsorption process.

INTRODUCTION

The prehydrolysis kraft process is a well-established process for the production of high purity dissolving pulps. In a first step, denoted as autohydrolysis or prehydrolysis, wood is treated with water in order to dissolve hemicelluloses that are hardly solubilized in an alkaline kraft cooking step. In subsequent kraft cooking the hemicellulose content is further reduced to about 3% xylan for hardwood pulps. The hemicellulosic fraction dissolved during autohydrolysis of hardwoods is of particular interest as a source of xylooligosaccharides and platform chemicals derived thereof. Efforts toward the utilization of this fraction date back to the 1930s.[1,2] However, at present water prehydrolysis is not commonly implemented in industrial practice due to the formation of highly reactive lignin precipitates that cause severe plugging problems.[3,4]

Several procedures for the lignin removal from autohydrolyzates are described in literature. These processes demand cooling of the hydrolyzates to temperatures of at least below 100 °C where lignin precipitation already causes incrustation of the equipment. The adsorption of lignin from autohydrolyzates on activated charcoals at temperatures ranging from 20 to 60 °C proved to be a suitable method for lignin removal.[5] However, the prevention of lignin scaling only became possible when lignin adsorption was implemented at prehydrolysis temperature.[6] During the so-called HiTAC process (high temperature adsorption on activated charcoal) the lignin is adsorbed directly after prehydrolysis at hydrolysis temperature. It exhibits a fairly good selectivity toward lignin adsorption without concomitant adsorption of carbohydrates up to a lignin removal of 85% at 170 °C. At charcoal concentrations exceeding a concentration of 20 g L^{-1} oligomeric carbohydrates are increasingly adsorbed, while monomeric sugars remain unaffected. The carbohydrate dehydration products, furfural, and HMF, are removed during the AC treatment to a sufficiently low concentration level which allows an uninhibited fermentation of the hydrolyzate. The equilibrium adsorption time is reached within a rather short period of time. It was shown that adsorption is significantly more efficient at autohydrolysis temperature (150 and 170 °C) than at room temperature, which is advantageous for purifying the hydrolyzate during its discharge from the digester. Lignin adsorption is highly dependent on the charcoal used. The choice of an activated charcoal of high microporosity and surface area is indispensable for a successful implementation in industrial practice.[6] A cost-effective regeneration process for the charcoal is needed for a commercial realization. Thus, it is the scope of this work to develop an appropriate recycling strategy for the exhausted charcoal derived from the HiTAC process.

Various studies of adsorption and desorption of substituted phenolic compounds on charcoal are known due to their ubiquitous occurrence in waste waters.[7] Based on the fact that lignin is built of phenolic subunits—although highly macromolecular and therefore distinctly different in behavior—it is assumed that some processes for phenol desorption are applicable for prehydrolysis-lignin desorption from charcoal. In their review on the adsorption of phenolic compounds on activated charcoal, Dabrowski et al.[8] depict the influence of various process parameters on adsorption behavior. These parameters include the type of activated charcoal, surface functionalities, pH, the oxygen availability, and potential electrolyte addition. An important aspect of substituted phenol removal is the irreversible adsorption onto the charcoals. The inductive effect of methoxyl- and ethoxyl substituents leads to a

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strong binding of phenols to the charcoal matrix and to a high degree of irreversible adsorption.[8] Increasing temperature and adsorption time further enhances chemisorption of phenols and leads to polymerization reactions on the charcoal.[8] These effects are likely to occur in the HiTAC-process as well, because autohydrolysis lignin shows a high degree of methoxyl-groups (20%[9]) and adsorption temperature is high (170 °C). Further interaction mechanisms described are donor−acceptor interactions between the aromatic ring and alkaline surface groups such as carbonyls, dispersion effects, and electrostatic attraction.[7]

Processes for phenol desorption include thermal desorption and solvent extraction,[10,11] as well as microwave regeneration.[12] Microwave regeneration utilizes the fact that charcoals have dielectric properties that absorb microwave energy and convert it to thermal energy. Chang et al.[12] successfully implemented microwave irradiation for the removal of an azo dye from charcoals. Thus six adsorption/desorption cycles could be performed without capacity losses. Anionic and cationic surfactants find application for the desorption of benzodiamine dyes in a process called surfactant enhanced carbon regeneration (SECR). Anionic surfactants SDS (sodium dodecyl sulfate) and AOT (sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate) showed a considerably better performance than their cationic counterparts and led to a desorption of 40−65% benzodiamine.[13] Solvent extraction with dichloromethane/methanol (93:7) at 140 °C was effective for the recovery of chlorinated phenols up to an efficiency of 75%, although short desorption times (5 min) where applied, due to degradation of the products.[10] Ethanol found application in the desorption of pomace from charcoal. Although desorption efficiency was only about 20%, five successful adsorption/desorption cycles were performed.[11]

If the desorption of matter is not efficient any more, spent charcoals are either burnt for energy generation or thermally regenerated. Thermal regeneration is performed in furnaces at temperatures of up to 1500 °C, but the rather moderate temperature range of 800−1000 °C is more commonly used.[14] Conventional oxygen-free regeneration processes consist of a drying step at 105 °C, a pyrolysis step under inert atmosphere at temperatures of 650−850 °C, and a carbonization step with CO_2, steam, or a combination of both at 650−850 °C.[15] Steam is applied for the removal of volatile organic compounds and enhances regeneration in a way that treatment temperatures, and therefore costs, can be reduced significantly.[16] Regeneration of charcoal saturated with benzene and toluene is even possible at temperatures of only 250−350 °C in oxygen-containing atmosphere. Generally, adjusting the oxygen content during the carbonization step is a plausible means to tailor the regenerated activated carbon. Regeneration efficiency is highly dependent on the type of charcoal, the adsorbed substances, and the process chosen and can yield up to 100%.[17]

The thermal regeneration step is similar to activated charcoal production. Traditional precursors for activated charcoal production are coal, coconut shells, lignite, wood, and peat.[18] In recent years various other materials, including cellulose,[19] hydrolysis lignin,[20] and kraft lignin[21,22] have been successfully tested for charcoal production. Thus, a thermal regeneration step of the charcoal derived from the HiTAC-process (a lignin loaded charcoal) might yield an additional amount of charcoal due to lignin conversion to activated charcoal.

This paper aims at the development of adequate recycling and regeneration strategies for spent activated charcoals from the HiTAC-processing of *Eucalyptus globulus* autohydrolyzates. Solvent extraction and thermal regeneration of spent charcoals were applied in order to regenerate a charcoal of high surface area and microporosity that can be recycled efficiently in the HiTAC-process. Solvent extraction was chosen as a rather simple regeneration method that does not require extensive process equipment. Since solvent extraction did not show the desired effects, thermal regeneration of the charcoals was performed according to the literature[14] using CO_2 as active agent. Thermal regeneration using O_2 as active agent at low temperatures, like it was successfully tested for phenol desorption,[17] was tested as a cost-effective alternative.

This study includes performance tests of the regenerated carbons and a detailed characterization of the resulting hydrolyzates.

■ MATERIALS AND EXPERIMENTAL METHODS

Autohydrolysis and HiTAC-Processing. Autohydrolysis and subsequent HiTAC-processing of the hydrolyzates was carried out according to Gütsch and Sixta.[6] The experiments were carried out in a lab-scale Parr reactor station with a reactor volume of 450 mL, mechanical stirring, and temperature control. A 50 g sampling of Eucalyptus globulus wood chips was placed inside one reactor. Deionized water was added to achieve a liquor-to-wood ratio of 5:1. The reactor was heated up to 170 °C within 30 min (minimum heating time), the temperature was maintained until a prehydrolysis-factor (P-Factor) of 600 h was reached (corresponding to approximately 60 min). The P-factor was calculated from the recorded temperature/time data according to Sixta[23] on the basis of an activation energy of 125.6 kJ mol^{-1}. The autohydrolyzate was subsequently separated from the wood residue by displacement with nitrogen to a preheated second reactor containing saturated steam with a temperature of 170 °C and 5 g of powdered activated charcoal (Sigma decolorizing purchased from Sigma-Aldrich). The isothermal phase separation recovered all components that are dissolved in the autohydrolyzate at 170 °C, particularly the components that are insoluble at lower temperatures. During this separation step no temperature and pressure drop occurred. The reactor containing charcoal was held at autohydrolysis temperature for 10 min adsorption time. Subsequently, the reactor was cooled down to below 30 °C with ice water. The spent charcoal was separated via vacuum filtration using a 0.45 μm polyamide membrane. The experiment was performed five times. For the regeneration experiments the spent activated charcoal of these five experiments was mixed and oven-dried at 55 °C before regeneration to allow an even substrate. The process was repeated with the charcoal after thermal regeneration.

Solvent Desorption. A 1 g sample of spent activated carbon was suspended in 5 mL of the solvent (0.5 N NaOH, acetone/water 5:1 (v/v), ethanol, acetic acid, DMSO) and shaken at room temperature overnight. AC was separated via a 0.45 μm filter and washed with 100 mL of deionized water.

Thermal Regeneration of Spent Activated Charcoal. A 5 g sample of spent activated charcoal was weighed in a sagger and placed in a tube furnace. The furnace was heated under nitrogen (24 L h^{-1}) at a rate of 3 °C min^{-1} to the regeneration temperature (850 and 950 °C). Carbonization was performed at the regeneration temperature for 30 and 45 min, respectively using carbon dioxide (24 L h^{-1}). Subsequently the charcoal was cooled under nitrogen (24 L h^{-1}) overnight.

One regeneration experiment was performed with air as oxidizing agent. Therefore activated charcoal was heated in the furnace at a rate of 3 °C min^{-1} under air atmosphere to 300 °C. Temperature is held for 30 min. Subsequently, the charcoal was cooled under air overnight.

Analytical Methods. Lignin content was analyzed via UV/vis-spectrometry (absorption coefficient of 110 L g^{-1} cm^{-1} at 205 nm according to Tappi um-250.[24] Furfural and hydroxymethylfurfural (HMF) were quantified via HPLC on a Hypersil ODS column with UV detection at 277 nm with 14% (v/v) acetonitrile as eluent at a temperature of 65 °C.

The carbohydrate content and the composition of the samples were analyzed before and after a two-stage total hydrolysis with sulfuric acid by high performance anion exchange chromatography with pulsed amperometric detection.[25]

All concentrations are calculated in relation to the wood inserted in the autohydrolysis stage and are given in % oven dry wood (%odw).

Size exclusion chromatograms (SEC) were obtained on a PSS MCX 1000 (8 × 300) column coupled with RI detection and 0.1 M NaOH as eluent.

BET was measured on a BELsorp mini II from BEL Inc., Japan, according to Brunauer et al.[26] and IUPAC recommendations.[27] Pore distributions were plotted in terms of the BHJ- and the MP-plot for meso- and micropores, respectively.

■ RESULTS AND DISCUSSION

Activated charcoals with a highly microporous structure, small mesopore diameters and a low number of mesopores show the best selectivity toward lignin adsorption.[28,6] Therefore an activated charcoal that fulfils these prerequisites was chosen for the adsorption and desorption experiments. The removal efficiency and selectivity of lignin-derived compounds from 170 °C hot autohydrolyzates proved to be optimal at a charcoal dosage of 20 g L^{-1}.[6] Under these conditions 75% of the released lignin was removed from the autohydrolyzate, whereas the concentration of carbohydrates remained substantially unchanged. Along with lignin removal major amounts of the carbohydrate degradation products furfural and HMF were adsorbed, which is advantageous for a subsequent biotechnological treatment.[29] Thus, a fresh charcoal concentration of 20 g L^{-1} was used for the production of spent charcoals from the HiTAC process for the regeneration experiments. The lignin-loaded activated carbon was separated from the hydrolyzate by vacuum filtration using a 0.45 μm polyamide membrane, resulting in the total separation of the charcoal and a clear hydrolyzate. On average, 75% of the released lignin was adsorbed by fresh activated charcoal representing a lignin reduction from 5.3% odw to 1.3% odw. The same procedure without activated charcoal resulted in a slight reduction of the lignin content of about 0.5%, for example, from 5.3 to 4.8% odw.

The fresh activated charcoal exhibited a specific surface area of 880 m^2 g^{-1} and a high proportion of small micropores with a pore diameter d_p < 0.1 nm. After HiTAC-processing (high temperature adsorption on activated charcoal) of the hydrolyzates and water washing of the activated charcoal, its specific surface area was reduced to 70 m^2 g^{-1} (Table 1) which is considerably lower as compared to that being used in wastewater treatment. Fresh carbons from wastewater treatment have a BET surface area of about 900 m^2 g^{-1} and are regenerated when the BET surface area falls below 600 m^2 g^{-1}.[16] The low surface area of spent activated charcoals derived from the HiTAC-process was probably due to lignin polymerization catalyzed by the activated carbon under the conditions occurring during the adsorption step.[8,9]

Table 1. BET Surface after Solvent Desorption of Lignin

solvent	dissolved lignin (% lignin on AC)	BET (m^2 g^{-1})
water		70
NaOH (0.5 N)	10	109
acetone/water (5/1)	21	122
ethanol	10	95
acetic acid	18	106
DMSO	n.d.[a]	134

[a] n.d. = not detected.

Solvent Desorption. A rather simple way to reutilize the charcoal would be a washing step using water or a lignin solvent. Simple washing of the activated charcoal with water removed only 2.5% of the adsorbed lignin and did not restore the adsorption capacity of a fresh activated carbon (Figure 1a). The lignin content in the autohydrolyzate was 4% odw after the first reutilization of the water washed activated charcoal and thus substantially higher as compared to the lignin content obtained after the treatment with fresh activated carbon. The lignin adsorption capacity of the recycled water-washed activated carbon (simply referred to as spent AC) was proportional to its low BET surface area (69 m^2 g^{-1}). On the basis of the results it can be concluded that simple reutilization of charcoal after water washing is not applicable in industrial practice due to the low washing efficiency.

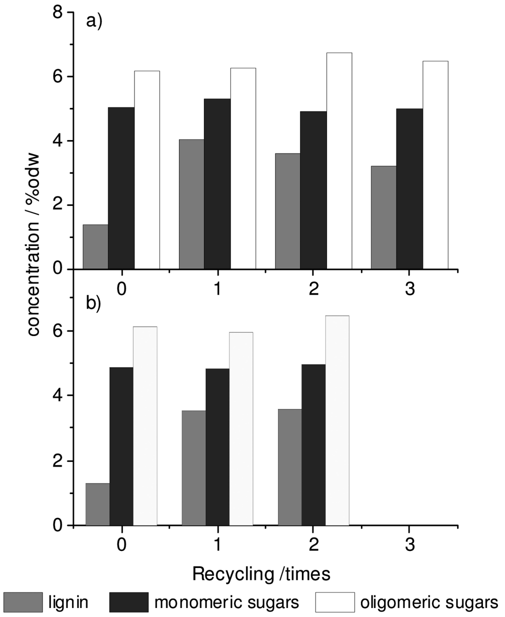

Figure 1. Composition of autohydrolyzates using recycled charcoals: (a) after pure water washing of the charcoals, (b) after washing the charcoals with acetone/water (5/1).

The desorption of lignin by dissolution using various lignin solvents led to a lignin removal of 21% at most (Table 1). Although the active surface area was thereby enhanced to some extent, it is still far below an appropriate range for efficient further lignin adsorption, probably due to the high binding strength of the remaining lignin to the charcoal and due to the inaccessibility of lignin in the pores, which was also reported by

Table 2. Regeneration of Spent Activated Charcoals

			regenerated AC				
	fresh AC	spent AC	1	2	3	4	fresh AC regenerated
regeneration time (min)			30	45	30	30	30
regeneration temperature (°C)			850	850	950	300	950
atmosphere			CO_2	CO_2	CO_2	air	CO_2
yield (% spent AC)			77.3	76.0	68.4	83.3	
yield (% fresh AC)			108.3	106.4	95.7	116.7	83.3
BET (m^2 g^{-1})	880	69	605	641	830	568	1075

Dabrowski et al.[8] The highest surface areas were achieved by the extraction of the loaded activated charcoal with DMSO (134 m^2 g^{-1}) and an acetone/water (5/1) mixture (122 m^2 g^{-1}). However, when reused in the HiTAC-process, only minimal lignin adsorption was observed, which was rather comparable to lignin adsorption after pure water washing (Figure 1b). The tendency of decreasing lignin content after repeated recycling that was observed after water washing was not observed using acetone/water mixtures. Sodium hydroxide is a classical solvent for lignin and easily removes prehydrolysis lignin from reactor equipment, even after a prolonged temperature treatment and the formation of highly polymerized lignin.[30] Nevertheless, subjected to spent AC, only minor amounts of surface lignin are solubilized. Although literature reports beneficial effects of ethanol extraction for phenolics removal,[11] no such effect was observed for HiTAC-treated charcoals. It can be assumed that lignin solvents other than the ones tested, for example, ethylacetate and ionic liquids, are not capable to fully dissolve the highly polymeric lignin in the charcoal pores either. In summary, solvent extraction is not a viable recycling technology to restore the adsorption capacity of activated carbon following a HiTAC treatment of autohydrolyzates.

Thermal Regeneration. Hence spent charcoals were thermally reactivated at 850 and 950 °C and carbonization times of 30−45 min under CO_2-atmosphere. In an effort to reduce energy input a regeneration procedure using air as oxidizing agent at a carbonization temperature of 300 °C was also conducted. The conditions and results of the thermal regeneration trials are summarized in Table 2. Thermal treatment at 850 °C for 30 min increased the specific surface area of the activated carbon to 605 m^2 g^{-1} and further to 641 m^2 g^{-1} when prolonging the reaction time to 45 min. The yield of the recycled activated carbons was 106 and 108%, respectively, obviously owing to the partial conversion of the adsorbed lignin into activated carbon. Therefore more drastic conditions including longer regeneration times and/or higher temperatures were applied hoping to attain the full adsorption capacity of the recycled activated carbon. A higher regeneration temperature of 950 °C led to a surface area close to that of the fresh carbon (830 m^2 g^{-1} vs 880 m^2 g^{-1}), while the yield of the recycled activated carbon was still 96%. Subjecting a fresh sample of activated carbon to the same treatment conditions (950 °C, 30 min) resulted in a yield of only 83%. However, this mass loss was clearly compensated by a drastic increase of the BET surface area to 1075 m^2 g^{-1} (+ 22%). These results allow two possible explanations: (1) the lignin on the spent AC is not simply removed from the coal, but transformed to charcoal of a considerably high surface area; (2) the lignin attached to the spent AC protects the AC from thermal degradation, but is itself totally removed within the thermal regeneration step. Because the lignin is used as a raw material for charcoal production,[20] it is, however, assumed that the former explanation is more reliable.

Distinct differences between the charcoals exist in their micropore (Figure 2) and mesopore (Figure 3) distributions.

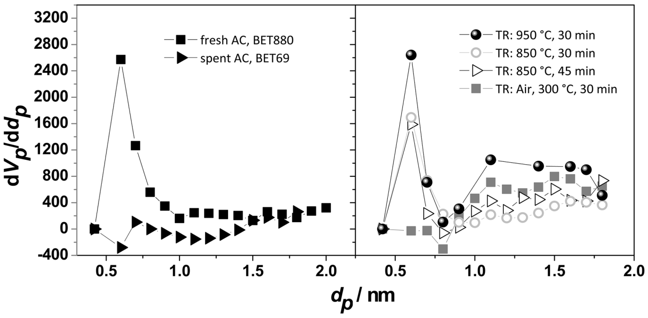

Figure 2. Micropore distribution of (a) fresh and spent AC and (b) thermally regenerated charcoals.

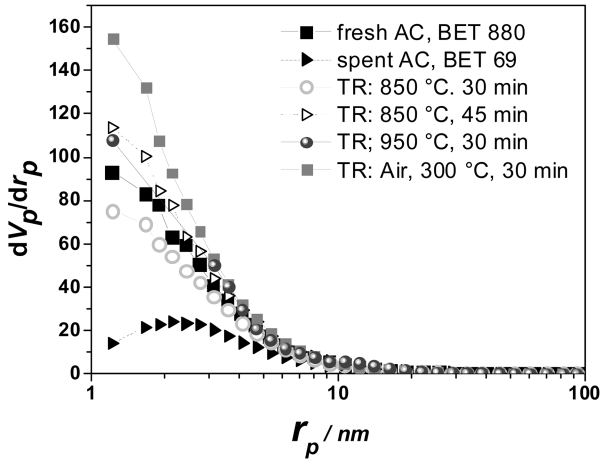

Figure 3. Mesopore distribution of thermally regenerated charcoals.

The original charcoal showed a high fraction of small sized micropores (d_p < 1 nm) and small mesopores (r_p = 1−10 nm), while the spent activated charcoal was lacking small micropores and contained less and smaller mesopores. Obviously, those sites were preferably occupied by firmly attached lignin moieties as indicated by the high resistance toward solvent extraction. Thermally reactivated charcoal at 850 °C showed a pore distribution similar to the original charcoal, but exhibited a lower volume of small micropores. A meso- and micropore distribution almost identical to that of fresh carbon was achieved by regeneration at 950 °C for 30 min. Interestingly, when fresh charcoal was subjected to these thermal regeneration conditions, the amount of small micropores was

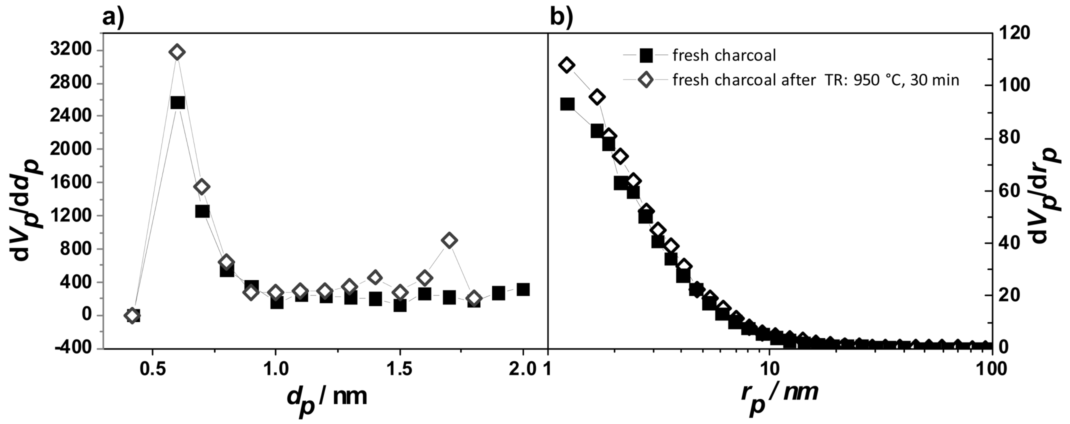

Figure 4. (a) Micropore distribution and (b) mesopore distribution of fresh charcoal and after thermal regeneration of fresh charcoal.

drastically increased which in turn resulted in a significant rise in the BET surface area (Figure 4).

Reutilization of the thermally reactivated charcoals showed that the specific lignin adsorption capacity can be described sufficiently well by the specific surface area of the charcoals (Figure 5). An effect of pore size distribution on lignin adsorption however was not observed. The charcoal that was regenerated at 950 °C for 30 min revealed a specific lignin adsorption capacity comparable to that of a fresh sample. There, both the BET surface area as well as the pore size distribution profile could be fully restored. All other charcoals had a decreased capacity for lignin adsorption, in agreement with their reduced overall surface area.

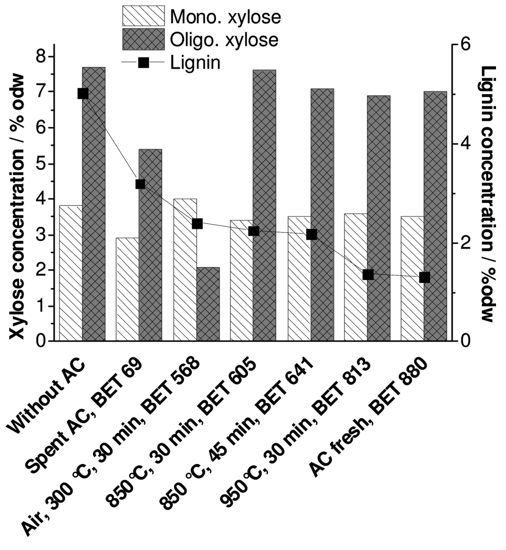

Figure 5. Lignin and carbohydrates in the HiTAC-treated hydrolyzates using thermally regenerated charcoals.

Generally the charcoals regenerated at 850 and 950 °C showed a high selectivity toward lignin, nevertheless up to 10% xylooligomers and up to 8% monomeric xylose were adsorbed using both fresh and thermally regenerated charcoals (Table 3). All other carbohydrate components ($\sum < 3\%$ odw) were not adsorbed. The xylan degradation products furfural and acetic acid were removed from the liquor to a similar extent using fresh and regenerated charcoals, respectively. In summary, the charcoal regenerated at 950 °C for 30 min behaved completely similar to fresh AC in all aspects investigated and can therefore easily be recycled in the HiTAC process.

The regeneration experiment performed at 300 °C in oxygen-containing atmosphere exhibited a rather low total surface area of the resulting charcoal (568 $m^2 g^{-1}$), but the yield of the charcoal was high and exceeded 100% of the original AC. Therefore it was expected, that more severe treatment conditions and an optimized gas flow in an oxygen containing environment could still increase the surface area while maintaining an acceptable yield level. However, the charcoal showed a completely different pore size distribution as compared to the charcoals regenerated in CO_2-atmosphere: the amount of small mesopores (r_p, 1−10 nm) and large micropores (d_p, 1−1.7 nm) was distinctly increased, but the high number of small micropores (d_p < 1 nm) was not restored. Thus the micropore structure resembled that of spent AC. Obviously, the combination of oxygen-containing atmosphere and low temperatures was not able to convert the polymerized lignin moieties to a microporous charcoal. Instead, it widened the mesoporous structure. When reutilized in the HiTAC-process, this charcoal showed a lignin adsorption proportional to its BET surface area, but also severe adsorption of oligomeric xylose (72%). The formation of mesopores instead of micropores may thus be a reason for the loss in selectivity during the HiTAC-process. Further, the treatment in oxygen-containing atmosphere possibly initiates the formation of carboxylic surface groups that might favor the adsorption of carbohydrates.[31] Thus, although the yield of thermal regeneration under oxygen atmosphere is high, modification of the process in terms of higher regeneration temperatures and longer regeneration times will not lead to satisfying results due to the formation of high amounts of mesopores without the formation of micropores.

■ CONCLUSIONS

Adsorption of lignin and furanic compounds from prehydrolysis-kraft prehydrolyzates on activated charcoals at high temperatures may be considered as a selective process for the prevention of incrustations and allows the unrestricted utilization of the prehydrolyzate carbohydrate fraction. To promote an economically viable process, regeneration possibilities of the spent charcoals were evaluated and an efficient regeneration process was developed. While solvent treatment of the spent charcoals was not sufficient for removing the lignin, thermal treatments efficiently regenerated the spent activated charcoals at temperatures exceeding 800 °C. Thermal

Table 3. Reutilization of Thermally Regenerated Charcoals: Composition of Hydrolyzates

			regenerated charcoal				
	without charcoal[a]	fresh charcoal	1	2	3	4	spent charcoal
BET ($m^2\ g^{-1}$)		880	605	641	830	568	69
Composition of Hydrolyzates (% odw)							
lignin	5.04	1.31	2.25	2.19	1.38	2.41	3.20
Monomeric Carbohydrates (% odw)							
glucose	0.2	0.1	0.1	0.1	0.1	0.2	0.1
xylose	3.8	3.5	3.4	3.5	3.6	4.0	2.9
mannose	0.1	0.1	0.1	0.1	0.1	0.1	0.1
arabinose	0.3	0.3	0.3	0.3	0.3	0.3	0.2
rhamnose	0.2	0.2	0.2	0.2	0.2	0.2	0.1
galactose	0.7	0.7	0.6	0.6	0.7	0.7	0.5
Oligomeric Carbohydrates (% odw)							
glucose	0.4	0.4	0.4	0.4	0.4	0.4	0.3
xylose	7.7	7.0	7.6	7.1	6.9	2.1	5.4
mannose	0.4	0.3	0.4	0.4	0.3	0.4	0.3
arabinose	0.0	0.0	0.0	0.0	0.0	0.0	0.0
rhamnose	0.1	0.1	0.1	0.1	0.1	0.1	0.1
galactose	0.4	0.3	0.3	0.3	0.3	0.3	0.2
Carbohydrate Degradation Products (% odw)							
furfural	0.7	0.3	0.2	0.2	0.2	0.4	0.6
HMF	0.1	0.0	0.0	0.0	0.0	0.1	0.1
free acetic acid	n.d.	2.3	2.4	2.5	2.4	2.6	2.0
bound acetic acid	n.d.	1.3	1.3	1.2	1.3	1.3	1.0

[a] n.d. = not detected.

regeneration at 900 °C for 30 min under CO_2 atmosphere showed the best performance: An active surface area, selectivity, and adsorption capacity during reutilization comparable to that of fresh charcoal were achieved. The yield of the thermal regeneration of the spent charcoal was even higher (on average 100%) as compared to thermal regeneration of the fresh carbon. This allows two conclusions: the protection of the coal by lignin that is totally removed during regeneration, and the (partial) transformation of lignin to charcoal during the regeneration process.

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Notes

The authors declare no competing financial interest.

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Paper V

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Short Note

New aspects of residual lignin isolation

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Keywords: acidolysis; alkaline extraction; hexenuronic acid; NMR; Ox-Dem kappa; residual lignin; soda-anthraquinone (soda-AQ).

Introduction

Isolation of lignin from its polysaccharide matrix in wood or pulp is an inevitable prerequisite for its complete structural characterization. A commonly applied method of lignin isolation from wood feedstock is the extraction of milled wood lignin (Björkman 1956). The isolation of dissolved wood lignin is a rather new method (Fasching et al. 2008). Isolation of lignin from wood and pulp by acidolysis is simple and rapid (Gellerstedt et al. 1994; Evtuguin et al. 2001) and the resulting acidolysis lignin (AL) is of high purity. Enzymatic hydrolysis (Yamasaki et al. 1981; Chang 1992) and the combined method of enzymatic mild acidolysis (Argyropoulos et al. 2000) are suited for lignin isolation from pulp.

The structure of AL from *Eucalyptus globulus* kraft pulp was intensely investigated by Duarte et al. (2000) and Pinto et al. (2002). AL contained less etherified units and more free phenolic functions as compared to native lignin and to enzymatically isolated lignin from *E. globulus* kraft pulps. Accordingly, acidolysis could have split some β-O-4 bonds (Duarte et al. 2000). Changes in lignin structure during isolation were further manifested in decreased molar mass of residual lignins isolated by acidolysis of softwood pulps (Al-Dajani and Gellerstedt 2002; Jääskeläinen et al. 2003). Additionally, AL from wood as well as kraft pulp contained some unsaturated structures and non-lignin materials of polysaccharide origin and condensed tannins of catechin and gallocatechin types (Gellerstedt et al. 1994; Evtuguin et al. 2001). Thus, applying an alkaline extraction (AE) prior to acidolysis of wood was suggested by Evtuguin et al. (2001) for removing these undesirable compounds. Rutkowska et al. (2009) applied this approach also for kraft pulp. Tannins are effectively removed during kraft pulping. At the end of washing, however, some lignin is reprecipitated on the pulp as a result of reduced alkalinity. Therefore, an alkaline extraction prior to lignin isolation might remove this precipitated lignin and render the isolated lignin more uniformly.

Within this study, the influence of AE prior to acidolysis as a means of increasing the comparability of lignins from differently pretreated sources was investigated. Residual lignin from a soda-anthraquinone (soda-AQ) pulp was isolated applying an acetone extraction (AcE) step to ensure complete removal of tannins and lipophilic extractives. Then an optional AE step followed before acidolysis. To investigate the degradation of lignin during the isolation in detail, lignin removal was followed in terms of kappa number, Ox-Dem kappa number, and hexenuronic acid (HexA) content. The high purities of the extracted lignins enabled reliable comparison of their structural compositions, which were evaluated by means of qualitative and quantitative NMR experiments, FT-IR spectroscopy, determination of sugar content, and wet chemical methoxy group determination, as well as elemental analysis. The results were recalculated in the C_{900} formula and discussed.

Experimental

Cooking experiments

Eucalyptus globulus wood chips from plantations in Uruguay were supplied by ENCE for soda-AQ continuous batch cooking (CBC) (Sixta et al. 2006) in a 10-l digester (H-factor 700, 94 min at T_{max} of 160°C) with synthetic cooking liquor (30.9 g l^{-1} effective alkali, 0.2% AQ on oven dry (o.d.) wood, alkali consumption 21%).

Lignin isolation and purification

Soda-AQ pulp (kappa 14) was subjected to AcE with a liquid-to-solid ratio (L/S) of 10 (SCAN-CM 2003). An optional AE was performed (0.3% NaOH, L/S 50, 1 h reflux, nitrogen atmosphere) and lignin was isolated via multistep acidolysis (Evtuguin et al. 2001).

Standard characterization

Carbohydrate content was evaluated after two-stage total hydrolysis by high performance anion exchange chromatography with pulsed amperometric detection (Sixta et al. 2001). Elemental analyses were performed by the Fraunhofer IAP. Standard protocols were used for determination of methoxy group content (Vieböck and Schwappach 1930), kappa number (Tappi 1993), Ox-Dem kappa number (Li and Gellerstedt 2002), and HexA content (Gellerstedt and Li 1996).

Table 1 Kappa, Ox-Dem kappa, and HexA contents at different extraction stages.

	Pulp preparation				
				Acidolysis	
	Soda-AQ Pulp	AcE	AE	With AE	Without AE
Total kappa	14.0	13.5	11.5	2.6	2.4
Ox-Dem kappa[a]	7.4	6.5	6.0	0.8	1.4
HexA[b]	27.2	27.9	29.3	–	–
(≈kappa)[c]	(2.3)	(2.4)	(2.5)		

[a]Kappa attributed to lignin (Li and Gellerstedt 2002). [b]HexA given in μmol g^{-1} o.d. pulp. [c]Kappa attributed to HexA (Li and Gellerstedt 1997). AcE, acetone extraction; AE, alkaline extraction.

Advanced lignin characterization

FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer using golden gate ATR. NMR spectra of the acetylated lignins (Lundquist 1992) were measured in $CDCl_3$ ($c=100$ mg ml^{-1} for ^1H and $^1H/^{13}C$ HSQC NMR experiments and $c=200$ mg ml^{-1} for quantitative ^{13}C NMR experiments) on a Bruker Avance DPX300 spectrometer (^1H 300 MHz, ^{13}C 75 MHz) using a 5-mm ^1H/BB inverse probe with z-gradient support, at 300 K. Chemical shifts were referenced to the residual solvent signals at $\delta(^1H)=7.26$ ppm and $\delta(^{13}C)=77$ ppm. Chromium(III)acetylacetonate (0.01 M) was added as relaxation agent for quantitative ^{13}C NMR experiments (Capanema et al. 2004). ^{13}C T_1 relaxation times were monitored with the inversion recovery technique for each sample. To ensure quantitative conditions, inverse-gated ^1H decoupled ^{13}C NMR spectra were recorded with 5 s relaxation delay, 0.4 s acquisition time, and 245 ppm spectral width. For each spectrum, 65 536 transients were accumulated. Quantitative ^1H NMR experiments were recorded with 7 s relaxation delay, 4.2 s acquisition time, and 26 ppm spectral width. In total, 128 scans were acquired from a sample with no added relaxation reagent. Processing of quantitative 1D spectra involved exponential window multiplication (LB = 0.3 Hz for ^1H and LB = 5 Hz for ^{13}C, respectively) of the free induction decay prior to Fourier transform. 2D $^1H/^{13}C$ HSQC NMR experiments were recorded with 2048 data points in the ^1H dimension, 512 time domain increments in the ^{13}C dimension, 256 scans, 0.5 s relaxation delay, 0.21 s acquisition time, and 16 ppm (^1H)/165 ppm (^{13}C) spectral width. 2D time domain data were multiplied with exponential (LB = 3 Hz; ^1H dimension) and shifted square sine bell (SSB = 2; ^{13}C dimension) functions and zero-filled to 2048 times 1024 real data points prior to Fourier transform. All 1D and 2D NMR data were processed and analyzed by Bruker software TopSpin 2.1.

Results and discussion

AcE led to a slight decrease of the soda-AQ pulp kappa number from 14 to 13.5. Subsequent AE yielded in a clear kappa number reduction of 2 units (Table 1). Regardless of whether AE was applied or not, kappa numbers of the pulps after acidolysis dropped to an average value of 2.5. As kappa number is not only affected by lignin, but by aliphatic double bonds, free aldehyde groups as well as by α-keto-carboxylic acids (Li and Gellerstedt 1998), the Ox-Dem kappa number has been introduced and represents the kappa number attributed to lignin only (Li and Gellerstedt 2002). Ox-Dem kappa dropped only slightly during AcE. AE reduced Ox-Dem kappa of the pulp by 0.5 units.

Within acidolysis of the pulps, similar amounts of lignin were removed as shown by equivalent Ox-Dem kappa reductions (Δ Ox-Dem kappa 5.2 with AE and 5.1 without AE). The pulp with AE finally showed a slightly lower Ox-Dem kappa number after acidolysis (Ox-Dem kappa 0.8) than the pulp without AE (Ox-Dem kappa 1.4). During acidolysis, the reduction in kappa number (Δ kappa 8.9 with AE, Δ kappa 11.1 without AE) was higher than the total Ox-Dem kappa value before acidolysis (Ox-Dem kappa 6.0 with AE and 6.5 without AE) (Table 1). Thus, substantial amounts of substances, which did not contribute to Ox-Dem kappa, were removed in addition to lignin within the step of acidolysis. Although similar amounts of lignin were removed from both pulps within acidolysis, the lignins showed different precipitation behavior in water during the recovery procedure. Lignin from alkaline extracted pulp precipitated only in minor amounts.

Thus, the step of AE mostly influenced the yield of lignin isolation and resulted in significant yield losses of 31% (Table 2). HexA contributed to approximately 2.5 kappa number units of each pulp, but generally do not contribute to Ox-Dem kappa value (Gellerstedt and Li 1996; Li and Gellerstedt 1997). The content of HexA remained unaltered during AcE and AE (Table 1), whereas it can be assumed that HexA was completely removed within acidolysis as the hexenuronic acid group is already liberated at slightly acidic conditions (Vuorinen and Alén 1998). Therefore, determination of HexA content after acidolysis was not accomplished.

Structural analyses of both lignin fractions with prior AE and without prior AE showed high similarities in lignin structure as can be seen from NMR (Table 3) and FT-IR spectra (Figure 1). Both isolation procedures yielded rather pure lignins with very low sugar content of approximately 1%, mainly glucose and xylose. Wet chemical methoxy group determination showed 1.12 (with AE) and 1.18 (without AE) methoxy groups per C_9 lignin unit. Similar tendencies were found in NMR determination of methoxy groups, but higher absolute values (1.22 with AE and 1.35 without

Table 2 Characterization of the isolated lignins with AE and without AE.

Lignin	Sugar (%)	Elemental analysis (%)					OMe (%)	C_{900} formula[a]	Lignin yield (mg g^{-1})
		C	H	N	O	S			
With AE	<1	60.4	5.9	0.2	33.3	0.2	17.3	$C_{900}H_{852}O_{306}(OCH_3)_{112}$	4.62
Without AE	1.2	58.4	5.7	0.2	29.7	0.2	17.6	$C_{900}H_{833}O_{270}(OCH_3)_{118}$	6.68

[a]Values are corrected for sugar impurities.

Table 3 Chemical shifts of resonances for integration of peaks in quantitative ^{13}C NMR spectra (Robert 1992; Ralph et al. 2004; Fasching et al. 2008).

	Chemical shift (ppm)		Lignin[a]	
Functional group	From	To	With AE	Without AE
Prim. aliph. OH	171.0	169.8	0.67	0.64
Sek. aliph. OH	169.8	168.8	0.29	0.29
Phenol. OH	168.8	167.5	0.42	0.49
O-subst. arom. C[b]	162.0	142.0	2.26	2.25
C-subst. arom. C[c]	142.0	125.0	1.82	1.84
H-subst. arom. C	125.0	101.5	1.91	1.91
β-β/α	86.0	85.2	0.04	0.02
β-O-4/β	81.0	79.8	0.13	0.13
Methoxy group	57.0	54.5	1.22	1.35

[a] ^{13}C integral area of the acetylated sample per aromatic unit normalized to the integral area corresponding to methoxy groups. [b] Non-etherified phenolic C-O-Ac added to integral area. [c] Non-etherified phenolic C-O-Ac deduced from integral area.

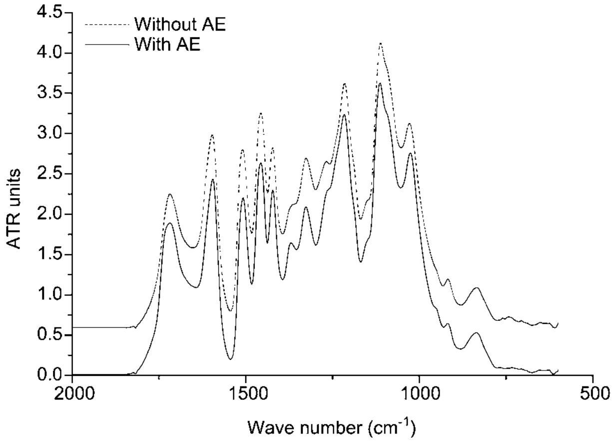

Figure 1 Attenuated total reflectance (ATR) FT-IR spectra of the isolated lignins with AE and without AE scaled on the 1503–1515 cm^{-1} band representing aromatic skeletal vibrations.

AE) were obtained. These values were in good agreement with those found by Duarte et al. (2000) for *E. globulus* kraft AL (1.2 methoxy groups per aromatic unit). The C_{900} formula was calculated from methoxy group content and elemental analysis and showed slightly higher oxygen and hydrogen contents for lignin with AE [$C_{900}H_{852}O_{306}(OCH_3)_{112}$] than the C_{900} formula $C_{900}H_{833}O_{270}(OCH_3)_{118}$ of lignin without AE (Table 2).

Structural analysis via HSQC and quantitative ^{13}C NMR experiments did not reveal any further differences between the isolated lignin fractions (Table 3). In addition to the common structural elements of lignins, NMR resonances at 7.24/105.6 ppm showed α-oxidized syringyl units, as were also found for lignins in soda-AQ pulping liquors (Venica et al. 2008). High intensities of carbonylic FT-IR bands at 1710 cm^{-1} (Figure 1) supported these findings. The presence of stilbene structures was indicated by NMR resonances in the ^{13}C range of 115–131 ppm and the ^{1}H range of 6.5–8 ppm (Ralph et al. 2004), as described by Rutkowska et al. (2009) for AL of *E. globulus* kraft pulp and Venica et al. (2008) for lignins in soda-AQ pulping liquors.

Conclusion

The effect of different treatments (acetone extraction and optional alkaline extraction) was studied in the context of residual lignin isolation from a *E. globulus* soda-AQ pulp by acidolysis. The results were monitored by determination of kappa number, Ox-Dem kappa number, and HexA content. During acetone extraction and alkaline extraction, lignin components were removed from the pulp. The residual lignins were of high purity and similar in chemical structure and composition with and without previous alkaline extraction. Alkaline extraction reduced the yield of isolated lignin significantly. Therefore, acetone extraction is a better and more efficient pretreatment step for acidolysis of *E. globulus* pulp.

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Veröffentlicht:

- — *mit internationalem Recherchenbericht (Artikel 21 Absatz 3)*
- — *vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eingehen (Regel 48 Absatz 2 Buchstabe h)*

(54) Title: PROCESS FOR IMPROVED PROCESSIBILITY OF HYDROTHERMOLYZATES OF LIGNOCELLULOSIC MATERIAL

(54) Bezeichnung : VERFAHREN ZUR VERBESSERTEN VERARBEITBARKEIT VON HYDROTHERMOLYSATEN VON LIGNOZELLULOSISCHEM MATERIAL

(57) Abstract: The present invention relates to a process for obtaining high-value products from lignocellulosic material, especially wood, comprising the steps of a) preliminary hydrolysis of the lignocellulosic material, b) removal of at least a portion of the hydrolyzate from the lignocellulosic material, c) direct adsorption of the encrustation formers from the hydrolyzate onto a suitable adsorbent and subsequently d) further processing of the hydrolyzate to obtain various products, for example from the oligosaccharides and monosugars, and acetic acid.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zur Gewinnung hochwertiger Produkte aus lignozellulosischem Material, insbesondere Holz, umfassend die Schritte: a) Vorhydrolyse des lignozellulosischen Materials, b) Abtrennung zumindest eines Teils des Hydrolysates vom lignozellulosischen Material, c) direkte Adsorption der Verkrustungsbildner aus dem Hydrolysat an einem geeigneten Adsorbens und nachfolgend d) Weiterverarbeitung des Hydrolysates zur Gewinnung vielfältiger Produkte, zum Beispiel aus den Oligosacchariden und Monozuckern sowie Essigsäure.

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Verfahren zur verbesserten Verarbeitbarkeit von Hydrothermolysaten von lignozellulosischem Material

Die vorliegende Erfindung bezieht sich auf ein Verfahren zur Gewinnung hochwertiger Produkte aus lignozellulosischem Material, insbesondere Holz, umfassend die Schritte:

a. Vorhydrolyse des lignozellulosischen Materials,
b. Abtrennung zumindest eines Teils des Hydrolysates vom lignozellulosischen Material,
c. direkte Adsorption der Verkrustungsbildner aus dem Hydrolysat an einem geeigneten Adsorbens und nachfolgend
d. Weiterverarbeitung des Hydrolysates zur Gewinnung einer Vielzahl an Produkten, zum Beispiel aus den Oligosacchariden und Monozuckern sowie Essigsäure.

Es ermöglicht die Weiterverarbeitung der mittels Hydrothermolyse aus dem lignozellulosischen Material gelösten Oligosaccharide und Monosaccharide zu hochwertigen Nebenprodukten und stellt somit einen weiteren Schritt zur vollständigen Verarbeitung aller Biokomponenten im Sinne einer Bioraffinerie dar. Neben der verbesserten Verarbeitbarkeit des Hydrolysates bietet der erfindungsgemäße Prozess die Möglichkeit der Entfernung furanosider Komponenten, die als Fermentationshemmer gelten.

Stand der Technik:

Hydrothermolytische Prozesse (Bobleter 2005) sind Prozesse, in denen reines Wasser in flüssiger Form oder als Dampf oder verdünnte oder konzentrierte Säuren eingesetzt werden, um lignozellulosisches Material unter erhöhter Temperatur aufzuschließen. Ohne die Anwendung von Vorbehandlungen oder den Einsatz weiterer Chemikalien ist es möglich, einen Teil der Biomasse als niedermolekulare Komponenten in Lösung zu bringen. Hydrothermolytische Prozesse finden als Vorbehandlung zur Zellstofferzeugung oder als Hauptprozessbestandteile bei der Fraktionierung von Biomasse Anwendung. Werden hydrothermolytische Verfahren als Vorbehandlungsschritt genutzt, so spricht man von Vorhydrolyse. Dient

Wasser als Agens, so spricht man auch von Autohydrolyse oder in flüssigem Aggregatszustand von Wasser-Vorhydrolyse.

Der Vorhydrolyse-Kraft Prozess ist ein weit verbreiteter Prozess zur Erzeugung von Chemiezellstoffen aus einer breiten Palette von Rohstoffen. Beim Kraft-Prozess handelt es sich um ein alkalisches Holzaufschlussverfahren. Weitere alkalische Prozesse der Chemiezellstofferzeugung stellen unter anderem der Vorhydrolyse-Soda- und der Vorhydrolyse-Soda-Anthraquinon-Prozess dar. Auch Vorhydrolyse-Organosolv-Prozesse sind in der Literatur bekannt.

Durch ein alkalisches Aufschlussverfahren allein ist es nicht möglich, Hemizellulosen in ausreichendem Maße aus dem Zellstoffverband zu lösen. Die Entfernung der Hemizellulosen ist allerdings eine wichtige Voraussetzung zur Herstellung von hochwertigen Chemiezellstoffen. Ein hochwertiger Chemiezellstoff zeichnet sich durch einen hohen Gehalt an α-Zellulose und einen geringen Gehalt an Hemizellulosen, d.h. von etwa 1 – 10 %, aus. Durch eine vor das Aufschlussverfahren geschaltete Hydrolyse ist es möglich, Hemizellulosen selektiv aus der Biomasse zu entfernen und so hochwertige Chemiezellstoffe herzustellen. Anwendung finden Chemiezellstoffe z.B. zur Herstellung von Celluloseacetat, Celluloseacetat-Filtertow für Zigarettenfilter und Ähnliches sowie von Viskose-, Modal- und Lyocellfasern.

Die Vorhydrolyse kann entweder in Form einer Autohydrolyse mit Wasser bei 160 - 180 °C oder in Form einer Hydrolyse mit verdünnter Säure (0,3 – 0,5 % H_2SO_4) bei 120 - 140 °C oder mit konzentrierter Säure (20 - 30 % HCl) bei etwa 40 °C durchgeführt werden (Sixta 2006).

Im Prozess der Vorhydrolyse werden die Hemizellulosen zu oligomeren und monomeren Zuckern abgebaut. Ein Großteil der Hemizellulosen ist hierbei Xylan und Glucomannan. Diese sind im Vorhydrolysat löslich und können zu hochwertigen Produkten der Nahrungsmittel- und Pharmaindustrie weiterverarbeitet werden. (Vázquez 2000; Huang 2008)

Aufgrund der Hochwertigkeit der Produkte und auf der Suche nach biogenen Ethanolquellen als Alternativtreibstoff sind viele Prozesse der Totalhydrolyse von Biomasse entwickelt worden, die auf denselben Prinzipien wie die Vorhydrolyse beruhen. In diesen Prozessen wird auch die Zellulose weitestmöglich abgebaut und ist somit nicht mehr zur Zellstoffgewinnung verwendbar. US Patent 5,503,996 (Torget 1996) beschreibt ein Vorhydrolseverfahren, indem sowohl Vorhydrolysat als auch zellulosischer Rückstand fermentativ aufgearbeitet werden.

Es ist bekannt, dass mit fortschreitender Hydrolyseintensität hochreaktive Substanzen gebildet werden. Diese Produkte zeigen eine hohe Tendenz, sich von der wässrigen Phase zu trennen und Verklebungen und Verkrustungen zu bilden, welche nur schwer zu kontrollieren sind und eine Nutzung des Vorhydrolysates erheblich erschweren. (Sixta 2006).

Es ist weiters bekannt, dass diese Verkrustungen aus Lignin und Ligninabbauprodukten gebildet werden. Lignin wird zu einem kleinen Teil während der Hydrothermolyse aus der Biomasse herausgelöst. Das Lignin liegt dann sowohl gelöst als auch kolloidal vor. Ablagerungen können sich sowohl aus dem kolloidalen als auch aus dem gelösten Lignin bilden. (Leschinsky 2008a; Leschinsky 2008b; Leschinsky 2009a; Leschinsky 2009b).

Die Vermeidung der Bildung dieser Ligninverbindungen wurde eingehend untersucht. Es wurde gezeigt, dass durch die Wahl der Wasservorhydrolyse-Bedingungen (Temperatur und Hydrolysedauer) die Ablagerungen nicht verhindert werden können. Niedrigere Temperaturen führen allerdings bei gleicher Hydrolyse-Intensität zu geringeren Mengen an gelöstem Lignin und daher auch zu einem geringeren Maß an Ablagerungen (Leschinsky 2008b).

Das Patent CS 248106 (Hojnos 1988) beschreibt die Verminderung der Ablagerungen durch die Verwendung einer sauren Vorhydrolyse bei geringeren Temperaturen (140 °C) als bei der konventionellen Wasservorhydrolyse (160 - 180 °C). Allerdings wird unter diesen Bedingungen grundsätzlich mehr Lignin gelöst als unter Wasservorhydrolyse-

Bedingungen. Dieses Lignin im Hydrolysat muss wiederum aufwendig entfernt werden, um die Hydrolysate zur Gewinnung von Stoffen aus den oligomeren und monomeren Zuckern nutzen zu können. Weiters werden unter den gewählten Bedingungen die Xylooligosaccharide zu Monozuckern abgebaut. Dies ist nicht immer erwünscht, da Xylooligosaccharide hochwertige Produkte darstellen.

Das Patent CS 228366 (Blazej 1982) beschreibt die Reduktion von Ablagerungen während der Vorhydrolyse von lignozellulosischem Material durch die Verwendung von Sulfit-Laugen welche mit Acrylamiden versetzt und mit SO_2 gesättigt sind, bei der Vorhydrolyse. Dies führt zu einer Reduktion der Ablagerungen um 12 %. SO_2 führt aber wiederum zur Lösung erheblicher Mengen an Lignin, wie bereits für den Zusatz von H_2SO_4 beschrieben.

IT 525470 (Rovesti 1955) beschreibt einen ähnlichen Prozess, in dem SO_2 während der Vorhydrolyse eingesetzt wird, um Ablagerungen zu vermindern. SU 1567700 (Kosheleva 1988) beschreibt einen 2-stufigen Hydrolyse-Prozess unter Einsatz von SO_2.

RO 93722 (Popescu 1985) beschreibt die Zugabe von Ammoniumlignosulfonat zu Holz-Vorhydrolysat nach erfolgter Furfuralentfernung, um ein Verstopfen der Anlagenteile bei den weiteren Verfahrensschritten zu vermeiden. Die weiteren Verfahrensschritte, die hier vor einer Verhefung des Vorhydrolysates nötig sind, bestehen aus der Neutralisation des Vorhydrolysates mit Kalziumhydroxid, Sedimentation sowie Nährstoff- und Hefezugabe.

Eine Vielzahl an Reinigungsmethoden zur Reinigung von Hydrolysaten wurde bereits untersucht. Diese Methoden zielen darauf ab, Inhibitoren aus den Hydrolysaten zu entfernen, um die zuckerreichen Hydrolysat-Lösungen einer anschließenden Fermentation oder enzymatischen Umsetzung zuzuführen. Als Inhibitoren werden in weiterer Folge Substanzen bezeichnet, die eine Fermentation oder enzymatische Umsetzung der Vorhydrolysate behindern.

Dazu zählen Lignin und dessen Abbauprodukte, insbesondere Furfural, Hydroxymethylfurfural sowie Essigsäure (Huang 2008).

Die meisten Prozesse zur Reinigung von Vorhydrolysaten, darunter auch der in CS 168207 (Hojnos 1972) beschriebene, verwenden mehrstufige Verfahren zur Reinigung der Vorhydrolysate. Zu den Verfahrensschritten zählen oft Filtrationen, Neutralisation (zumeist mit Kalkmilch), Eindampfung zur Entfernung flüchtiger Verbindungen (vor allem des Furfurals), Flockung und eine Vielzahl weiterer Verfahren zur fest-flüssig- und flüssig-flüssig-Trennung.

CN 101691587 (Yu 2009) beschreibt eine Extraktionsmethode, die eine Mischung aus Trialkylamin, n-Oktanol und Kerosin verwendet, um Inhibitoren aus sauren Vorhydrolysaten mittels flüssig-flüssig-Extraktion zu extrahieren. Ligninabbauprodukte werden dabei nur unvollständig aus dem Vorhydrolysat entfernt. Darüber hinaus sind die Nachteile des Einsatzes fossiler Chemikalien und deren Giftigkeit zu bedenken.

Es sind weiterhin Prozesse bekannt, in denen schwefelsaure Totalhydrolysate von einer Mischung aus Weichholz und pflanzlichen Abfallstoffen mit kationischen Polyelektrolyten behandelt werden, um Lignin-Bestandteile zu suspendieren und anschließend zu fällen. Die Lignin-Bestandteile dieser sauren Hydrolysate besitzen eine negative Oberflächenladung und können daher mit den kationischen Polyelektrolyten über elektrostatische Kräfte wechselwirken (Kholkin 1999). Autohydrolysate des Vorhydrolyse-Kraft-Prozesses hingegen zeigen annähernd keine Oberflächenladung und können daher mittels dieses Prozesses nicht aufgereinigt werden.

Zur Reinigung von Hydrolysaten wurde bereits eine Reihe von Adsorbentien untersucht. Die Adsorption erfolgt dabei zumeist bei Raumtemperatur oder knapp darüber. Ionenaustauscherharze und Aktivkohlen erbringen die besten Ergebnisse bezüglich der Entfernung von Inhibitoren (Moure 2006). Zur Entfernung von 60 - 70 % des Lignins werden 50 - 70 g Aktivkohle pro Liter Vorhydrolysat benötigt. Bei hohen Aktivkohlekonzentrationen tritt außerdem erhebliche Adsorption der Zucker etc. auf. (Parajo 1996; Xie 2005)

(Parajo 1996) untersuchte außerdem den Temperatureinfluss auf die Adsorption von phenolischen Bestandteilen (Lignin) aus Vorhydrolysat an Aktivkohle. Es konnte dabei gezeigt werden, dass mit steigender Temperatur die Adsorption von Lignin deutlich abnimmt. Dies steht in Einklang mit den gängigen physikalischen Grundsätzen, dass Adsorptionen exotherme Prozesse sind. Die Adsorption von Substanzen erfolgt daher bevorzugt bei geringen Temperaturen, zur Desorption muss dem System Energie zugeführt werden. Bei chemisorptiven Prozessen kann eine Aktivierungsenergie zur Adsorption nötig sein. Venkata Mohan (1997) postuliert anhand von Desorptionsexperimenten einen chemiesorptiven Prozess für die Adsorption von Lignin an Aktivkohlen. Die Notwendigkeit des Aufbringens von Aktivierungsenergie erscheint nach den Beobachtungen von (Parajo 1996) kontraproduktiv.

US 2009/0218055 A1 (Uusitalo 2009) beschreibt ein Verfahren zur Gewinnung von Hydrolyseprodukten. Eine Hydrolysat-Fraktion wird im Laufe dieses Prozesses in einem Tank bei hohen Temperaturen für die Dauer einer Kraft-Kochung aufbewahrt, um sie für weitere Hydrolysen zu nutzen. Eine mögliche und auch wahrscheinliche Bildung von Ablagerungen in diesem Aufbewahrungstank wird allerdings nicht berücksichtigt.

DE 10158120 A1 (Karstens 2003) beschreibt ein Verfahren zur Abtrennung von Xylose von xylanreichen Lignozellulosen und deren Weiterverarbeitung zu Chemiezellstoffen, basierend auf einer mechanischen Zerstörung der Holzhackschnitzel und anschließender Säure-Imprägnierung und Dampf-Vorhydrolyse. Xylose wird anschließend durch Waschung oder Zentrifugation des Holzes gewonnen. Durch die Säure-Imprägnierung werden die Xylane zu Xylose abgebaut. Es ist daher keine Gewinnung von Xylooligosachhariden möglich. Es wird berichtet, dass Lignin nicht in der Xylanlösung anfällt, dementsprechend befindet sich hochaktiviertes Lignin am Holz. Dies kann zu einem erhöhten Chemikalienverbrauch in Kochung und Bleiche führen.

Um die Vorteile eines Vorhydrolyse-Verfahrens nutzen zu können, ohne dabei die Nachteile von Verkrustungen und energieintensiver Eindampfung in Kauf nehmen zu müssen, beschreibt WO 94112719 (Wizani 1994) das Visbatch® Verfahren, das auf einer Dampfvorhydrolyse mit anschließender Neutralisation des kondensierten Hydrolysats im Kocher durch Kochlauge beruht. Die stoffliche Nutzung der durch die Vorhydrolyse gelösten Xylooligosaccharide ist bei diesem Prozess nicht möglich.

Angesichts des bekannten Standes der Technik bestand daher die Aufgabe, ein Verfahren zur Gewinnung von Produkten aus lignozellulosischem Material zur Verfügung zu stellen, das eine wirtschaftliche Gewinnung dieser Produkte in möglichst hoher Ausbeute und unter möglichst geringer Bildung von Verkrustungen, die durch das Hydrolysat hervorgerufen werden, ermöglicht.

Zusammenfassung der Erfindung

Diese Aufgabe konnte gelöst werden durch ein Verfahren zur Gewinnung hochwertiger Produkte aus lignozellulosischem Material, insbesondere Holz, umfassend die Schritte:

a. Vorhydrolyse des lignozellulosischen Materials,
b. Abtrennung zumindest eines Teils des Hydrolysates vom lignozellulosischen Material,
c. direkte Adsorption der Verkrustungsbildner aus dem Hydrolysat an einem geeigneten Adsorbens und nachfolgend
d. Weiterverarbeitung des Hydrolysates zur Gewinnung vielfältiger Produkte, zum Beispiel aus den Oligosacchariden und Monozuckern sowie Essigsäure,

wobei Schritt c. bei einer Temperatur des Hydrolysates von mehr als 60°C durchgeführt wird.

Es ermöglicht die Weiterverarbeitung der mittels Hydrothermolyse aus dem lignozellulosischen Material gelösten Xylooligosaccharide und Monosaccharide zu hochwertigen Nebenprodukten und stellt somit einen weiteren Schritt zur vollständigen integrierten Verarbeitung aller lignozellulosischen Komponenten im Sinne einer Bioraffinerie dar.

Unter Hydrothermolyse versteht man die Behandlung von lignozellulosischem Material in einem Druckreaktor mit Wasser oder verdünnten Säuren bei Temperaturen über 100 °C oder mit konzentrierten Säuren bei etwa 40 °C. Hydrolysat bezeichnet in diesem Zusammenhang die flüssige Phase, die dem heißen Reaktor nach erfolgter Hydrothermolyse entnommen wird.

Diese Abtrennung des Hydrolysates kann durch Ablassen des Hydrolysats oder durch Verdrängung des Hydrolysats durch ein Gas oder durch Verdrängung durch eine Flüssigkeit in einen zweiten Reaktor, Tank oder Adsorber erfolgen.

In dem zweiten Reaktor, Tank oder Adsorber befindet sich entweder schon vorher ein Adsorbens, oder dieses Adsorbens wird gleichzeitig mit oder sofort anschließend an die Hydrolysatüberführung zugegeben.

In einer bevorzugten Ausführungsform des erfindungsgemäßen Verfahrens erfolgt die Adsorption direkt nach der Abtrennung des Hydrolysates. Insbesondere ist es bevorzugt, dass zwischen Abtrennung der flüssigen Phase und Adsorption das Hydrolysat eine Temperatur von 100 °C nicht unterschreitet.

Günstig ist es insbesondere, wenn die Adsorption bei Temperaturen zwischen 100 und 190 °C stattfindet, bevorzugt sogar etwa bei der Temperatur der Vorhydrolyse.

Das Adsorbens wird ausgewählt aus der Gruppe von Substanzen, die selektiv Krustenbildner adsorbieren, d. h. die die Fähigkeit haben, selektiv Lignin, Ligninabbauprodukte und Dehydratisierungsprodukte der Kohlenhydrate (zum Beispiel Furfural und Hydroxymethylfurfural) bei Temperaturen zwischen 100 und 190 °C zu adsorbieren. Das Adsorbens ist vorzugsweise Aktivkohle.

Besonders bevorzugt wird eine Aktivkohle mit einer BET-Oberfläche > 600 m^2 g^{-1} eingesetzt.

Entgegen den physikalischen Grundsätzen, wonach Adsorptionen exotherme Prozesse sind und demnach bevorzugt bei niedrigen Temperaturen vonstatten gehen, und entgegen den Beobachtungen von (Parajo 1996), wurde überraschenderweise gefunden, dass die Adsorption der ligninartigen Bestandteile bei höheren Temperaturen in deutlich größerem Ausmaß erfolgt als dies bei Raumtemperatur und auch darüber hinaus unterhalb 60 °C der Fall ist. Zur Entfernung von 70 % - 90 % des Lignins werden mittels des erfindungsgemäßen Verfahrens lediglich 20 - 40 g Aktivkohle pro Liter benötigt. Dieser Wert liegt deutlich unter den oben genannten bisherigen Beobachtungen.

Durch das erfindungsgemäße Verfahren ist es möglich, alle zu Verkrustungen neigenden Komponenten zu binden und das Hydrolysat über längere Zeit bei hohen Temperaturen zu lagern, um z.B. eine Energierückgewinnung, z.B. über Wärmetauscher, zu ermöglichen. Dies war bisher nicht ohne das Inkaufnehmen hartnäckiger Ablagerungen möglich.

Die besonderen Vorteile des erfindungsgemäßen Verfahrens bestehen insbesondere darin, dass das Hydrolysat über dem Adsorbens ohne Bildung von Ablagerungen bei hohen Temperaturen für 0 – 72 Stunden gelagert werden kann und dass die Adsorption der Zucker < 20 % beträgt

Das erfindungsgemäße Verfahren ist unter anderem dadurch gekennzeichnet, dass die Vorhydrolyse bei einem Verhältnis von lignozellulosischem Material zu Hydrolysat in einem Bereich von 1:1 bis 1:10, bevorzugt von 1:2 bis 1:4, durchgeführt wird.

Zur Vorhydrolyse wird ein Verfahren ausgewählt aus der Gruppe bestehend aus Autohydrolyse mittels Wasser als flüssige Phase, saure Hydrolyse unter Zusatz von Mineralsäuren und saure Hydrolyse unter Zusatz von organischen Säuren.

Wenn Aktivkohle als Adsorbens verwendet wird, liegt bei Ligninadsorptionen bis 80 % die Adsorption von Zuckern unter 5 % und stellt damit eine wesentliche Verbesserung zu bekannten Verfahren dar. Der gesamte Zuckergehalt des Hydrolysates setzt sich aus monomeren und oligomeren Zuckern zusammen, wobei jedoch im erfindungsgemäßen Verfahren nur die oligomeren Zucker adsorbiert werden. Die monomeren Zucker bleiben in Lösung. Es ist daher bei Verwendung des erfindungsgemäßen Verfahrens in besonderem Maße möglich, eine sofortige Hydrolyse der oligomeren Zucker zu Monomeren direkt in Gegenwart von Aktivkohle durchzuführen, ohne wie bisher mit starken Verkrustungen rechnen zu müssen.

Um monomere Zucker als Produkt zu erhalten, kann zwischen Schritt c. und Schritt d. des erfindungsgemäßen Verfahrens zunächst eine Säure zum Gemisch aus Adsorbens und Hydrolysat zugegeben werden, um die oligomeren Zucker in monomere Zucker zu hydrolysieren, ohne mit starken Verkrustungen rechnen zu müssen. Anschließend wird das Adsorbens vom Hydrolysat abgetrennt.

Die erfindungsgemäße Adsorption führt zu klaren stabilen Lösungen, die nach der Adsorption und Abtrennung des Adsorbens eine Trübung von unter 10 NTU aufweisen. Hydrolysate, die nicht mit diesem Verfahren behandelt wurden, weisen Trübungen von weit über 10.000 NTU auf.

Das somit bereits gereinigte Hydrolysat kann anschließend Membranprozessen und enzymatischen oder fermentativen Prozessen zugeführt werden, um hochwertige Xylose- und Xylooligosaccharid-basierte Produkte zu erhalten.

In einer großtechnisch interessanten Anwendung des erfindungsgemäßen Verfahrens wird das vorhydrolysierte lignozellulosische Material zu Chemiezellstoff weiterverarbeitet.

Die Erfindung soll nun anhand von Beispielen erläutert werden. Diese sind als mögliche Ausführungsformen der Erfindung zu verstehen. Keineswegs ist die Erfindung auf den Umfang dieser Beispiele eingeschränkt.

Beispiele:

1. Allgemeiner experimenteller Teil

Eucalyptus globulus Hackschnitzel werden mit einer Schneidemühle gemahlen und fraktioniert. Die Fraktion zwischen 2,50 und 3,55 mm wird für die Vorhydrolyse verwendet. Die Vorhydrolyse und die Nachbehandlung/Adsorption (s.u.) wird in einer Laborreaktorstation unter ständigem Rühren (100 – 200 rpm) durchgeführt. Das Verhältnis von deionisiertem Wasser zu Holz beträgt 5:1. Um die Vorhydrolyse zu starten, wird der Reaktor schnellstmöglich auf eine Vorhydrolysetemperatur von 170°C aufgeheizt Die Temperatur wird bis zum Erreichen eines Vorhydrolyse-Faktors (P-Faktor) von 600 h auf dieser Temperatur gehalten. Wie in der Literatur beschrieben (Sixta 2006) wird der P-Faktor anhand der aufgezeichneten Temperatur- und Zeitdaten nach folgender Gleichung berechnet.

$$P = \int_{t_0}^{t} K_{rel.} \cdot dt = \int_{t_0}^{t} \frac{k_{(T)}}{k_{100°C}} \cdot dt = \int_{t_0}^{t} e^{(40.48 - \frac{15106}{T})} \cdot dt$$

Die relative Reaktions-Rate K_{rel} ist das Verhaltnis einer Reaktionsrate bei einer bestimmten Temperatur und der Referenz-Reaktionsrate bei 100 °C und ist gegeben durch:

$$\ln K_{rel.} = \ln \frac{k_{(T)}}{k_{100°C}} = \frac{E_A}{R \cdot 373{,}15} - \frac{E_A}{R \cdot T}$$

E_A ... Aktivierungsenergie
R ... Gaskonstante
T... Temperatur in Kelvin

Der P-Faktor ist die Fläche unter der Kurve von K_{rel} aufgezeichnet gegen die Hydrolysezeit.Für die Berechnung wird eine Aktivierungsenergie von 125,6 kJ mol^{-1} verwendet.

Anschließend wird das Vorhydrolysat unter Stickstoffdruck in einen zweiten, vorgeheizten Reaktor verdrängt. Dieser Reaktor ist mit gesättigtem Dampf bei 170 °C gefüllt, um eine isotherme Phasentrennung des Hydrolysates vom Holzrückstand zu ermöglichen. Optional ist der Reaktor mit 2 bis 36 g Aktivkohle gefüllt. Die Aktivkohlekonzentration wird im Folgenden durch das Verhältnis der Aktivkohlemasse zum Volumen der flüssigen Phase in der Vorhydrolyse in [g l^{-1}] angegeben. Die isotherme Phasentrennung führt dazu, dass keine unlöslichen Bestandteile am Holz verbleiben und damit beispielsweise in einer anschließenden Kochung weniger Kochchemikalien benötigt würden.

Nach der Phasentrennung wird im Reaktor für 0 - 80 Minuten eine definierte Temperatur von 120 - 170 °C gehalten. Dieser Schritt wird im Folgenden als Nachbehandlung bzw. bei Anwesenheit von Aktivkohle als Adsorption bezeichnet. Anschließend wird der Reaktor mit Eiswasser auf unter 40 °C gekühlt. Ist Aktivkohle im Reaktor enthalten, so wird diese sofort über einen 0,45 µm Filter im Vakuum abfiltriert. Die Lignin- und Trübungsmessungen finden direkt anschließend an die Vorhydrolyse-Versuche statt. Für alle weiteren Analysen wird das Vorhydrolysat bis zur Analyse bei 4 °C im Kühlschrank gelagert. Der Ligningehalt wird bei einer Verdünnung von 1:1000 mittels UV/Vis-Spektroskopie bei einer Wellenlänge von 205 nm unter Verwendung eines Absorptionskoeffizienten von 110 l g^{-1} cm^{-1} bestimmt (TAPPI 1991). Da die Furfuralabsorption bei 205 nm ein Minimum aufweist, kann der Furfuralgehalt der Lösungen bei dieser Wellenlänge vernachlässigt werden. Die Trübung wird mittels Hach 2100P Iso Turbidimeter bestimmt. Der Kohlenhydratgehalt und die Zusammensetzung der Kohlenhydrate des Vorhydrolysats wird vor und nach einer zweistufigen Totalhydrolyse mittels Hochdruck-Ionenaustausch-Chromatographie mit gepulster amperometrischer Detektion analysiert (Sixta 2001).

Die Größenausschlusschromatogramme (SEC) werden in 0,1 M NaOH als Laufmittel mittels einer PSS MCX 1000 (8x300)-Säule und RI-Detektion aufgenommen. Furfural und Hydroxymethylfurfural (HMF) werden mittels HPLC auf einer Hypersil ODS-Säule mit UV-Detektion bei 277 nm und 14 % (v/v) Acetonitril als Laufmittel bei einer Temperatur von 65 °C quantifiziert. Essigsäure wird mittels HPLC auf einer Rezex ROA-Säule mit RI-Detektion und 0,005 M H_2SO_4 als Laufmittel bei einer Temperatur von 65 °C bestimmt.

Die BET-Oberfläche der Aktivkohlen wird mittels BELsorp mini II von BEL Inc., Japan nach den Vorschriften von Brunauer, Emmett, Teller (1938) und IUPAC-Empfehlungen (Rouquerol 1994) ermittelt.

2. Referenzvorhydrolysen (Vergleichsbeispiele):

Die Vorhydrolysen werden wie unter 1. beschrieben ohne Zugabe von Aktivkohlen bei einer Nachbehandlungstemperatur von 170 °C und einer Nachbehandlungsdauer von 0, 20, 40 oder 80 Minuten durchgeführt. Der gemessene Gehalt an Lignin, oligomeren und monomeren Zuckern, Furfural, Hydroxymethylfurfural und Essigsäure ist aus Tabelle 1 ersichtlich.

Bei allen Versuchen, außer bei jenem mit sofortigem Abschrecken des Vorhydrolysates (d. h. Nachbehandlungsdauer von 0 Minuten), kommt es zu deutlichen Verkrustungen im Reaktor und am Rührer. Die Verkrustungen werden aus der Differenz des Ligningehalts zwischen der jeweiligen Nachbehandlung und der Vorhydrolyse bei sofortigem Abschrecken (Nachbehandlungszeit 0 Minuten) berechnet. Wie in Tabelle 1 aufgezeigt, steigt die Menge an Verkrustungen mit steigender Nachbehandlungsdauer deutlich an. Weiters werden mit steigender Nachbehandlungsdauer die oligomeren Zucker zu Monomeren und diese anschließend zu Furfural und HMF abgebaut. Daraus erklärt sich auch der sinkende Zucker- und steigende Furfural- und HMF-Gehalt. Weiters kommt es im Verlauf der Nachbehandlung zu einer Spaltung der Acetylgruppen der Xylooligomere und zu einem Anstieg der Essigsäurekonzentration.

Tabelle 1: Zusammenfassung der Referenzvorhydrolysen

Nachbehandlungs-Zeit	Ligningehalt in Lösung	Gesamtzucker (davon oligomere)	Furfural	HMF	Essigsäure	Verkrustungen
min	g l^{-1}	g l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	g l^{-1}
0	10,1	25,2 (16,1)	1166	113	2814	-
20	9,7	23,4 (13,1)	1555	172	3083	0,4
40	7,5	20,9 (9,7)	2304	237	3743	2,6
80	6,9	17,7 (4,6)	4257	426	4743	3,2

3. Einfluss der Aktivkohlekonzentration (erfindungsgemäße Beispiele)

Die Vorhydrolysen werden wie unter 1. beschrieben, jedoch unter Zugabe einer Aktivkohle, die durch eine BET-Oberfläche von 880 m² g^{-1} gekennzeichnet ist, bei einer Nachbehandlungstemperatur von 170 °C und einer Adsorptionsdauer von 20 Minuten durchgeführt. Aus Tabelle 2 ist die Zusammensetzung der Vorhydrolysate ersichtlich. Bereits ab einer Aktivkohlekonzentration von 8 g l^{-1} sind die Vorhydrolysate nach der Abtrennung der Aktivkohle klar und es treten keine Verkrustungen mehr auf. Ab einer Aktivkohlekonzentration von 8 g l^{-1} zeigen die Vorhydrolysate auch nach über 72 Stunden keine Eintrübung. Bei diesem Aktivkohlegehalt sind 44 % des Lignins im Vorhydrolysat adsorbiert. Ebenso wird eine HMF-Adsorption von 11 % festgestellt. Eine erste Adsorption der Zucker wird erst ab einem Aktivkohlegehalt von 24 g l^{-1} festgestellt. Dieser Gehalt entspricht einer Ligninadsorption von 84 %. Die Adsorption der Zucker erfolgt dabei hauptsächlich über die Adsorption der Oligosaccharide. Monosaccharide werden nicht adsorbiert. Während die Adsorption der wertvollen Zucker im gewählten Aktivkohlekonzentrationsbereich 20 % nicht überschreitet, werden Furfural und HMF mit steigender Aktivkohlekonzentration in steigendem Maße adsorbiert. Bei einer Aktivkohlekonzentration von 48 g l-1 sind 96 % des Lignins, 85 % des Furfurals, 71 % des HMF, und 19 % der Zucker adsorbiert. Essigsäure lagert sich nicht an die Aktivkohle an. Der Vergleich mit

Literaturwerten (Parajo 1996; Xie 2005) zeigt eine deutliche Verringerung der benötigten Aktivkohlemenge für die Ligninadsorption bei 170 °C im Vergleich zu Versuchen bei Raumtemperatur. Während gemäß Literatur eine Aktivkohlekonzentration von 50 - 70 g l^{-1} für die Adsorption von 60 - 70 % des Lignins benötigt wird, können mithilfe des erfindungsgemäßen Verfahrens bereits mit einer Aktivkohlekonzentration von 20 g l^{-1} 70 % des Lignins aus dem Vorhydrolysat entfernt werden.

Tabelle 2: Zusammensetzung der Vorhydrolysate nach Adsorption an Aktivkohle (BET 880 m² g-1)

Aktivkohle	Ligningehalt in Lösung	Gesamtzucker (davon Oligomere)	Furfural	HMF	Essigsäure
g l^{-1}	g l^{-1}	g l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
8	5,6	23,7 (12,7)	1477	153	3341
12	4,4	23,6 (13,1)	1167	127	3531
20	3,0	23,4 (13,7)	1068	137	3557
24	1,6	22,2 (11,6)	720	118	3496
32	0,9	20,7 (10,5)	333	71	3182
48	0,4	19,0 (6,9)	237	49	4175

4. Einfluss der Adsorptionsdauer (erfindungsgemäße Beispiele)

Die Vorhydrolysen werden wie unter 1. beschrieben unter Zugabe von 8 g l^{-1} einer Aktivkohle, die durch eine BET-Oberfläche von 880 m² g^{-1} gekennzeichnet ist, bei einer Adsorptionstemperatur von 170 °C durchgeführt. In Tabelle 3 ist die Zusammensetzung der Vorhydrolysate bei konstanter Aktivkohlekonzentration für unterschiedliche Adsorptionszeiten zusammengefasst. Aus den Daten geht hervor, dass bereits bei minimaler Adsorptionszeit eine fast vollständige Beladung der Aktivkohle erreicht ist. Die Dauer bis zur Erreichung des Adsorptionsgleichgewichts liegt daher deutlich unter jener, die für Adsorptionen unter 100 °C gefunden wurden (90 Minuten bis 24 Stunden). Mit anhaltender Adsorptionsdauer bei hohen Adsorptionstemperaturen werden die Zucker in zunehmendem Maße zu Furfural und HMF zersetzt (siehe dazu auch Beispiel 2 und Tabelle 1). Vergleicht man Tabelle 1 und Tabelle 3, so ist ersichtlich, dass auch die Zucker mit steigender Adsorptionsdauer nicht in steigendem Maße adsorbiert werden, sondern sich lediglich temperaturbedingt zersetzen. Auch die steigenden Furfural- und HMF-Werte sind darauf zurückzuführen, jedoch wird im Gegensatz zu den Zuckern ein Teil des Furfurals und HMF selbst bei der relativ geringen Aktivkohlekonzentration adsorbiert. Essigsäure wird nicht adsorbiert, im Gegenteil liegt sogar der Verdacht nahe, dass die Aktivkohle die Abspaltung der Acetylgruppen von den Xylanen katalysiert.

Tabelle 3: Einfluss der Adsorptionszeit auf das Adsorptionsverhalten

Adsorptionszeit	Ligningehalt In Lösung	Gesamtzucker (davon oligomere)	Furfural	HMF	Essigsäure
/ min	/ g l-1	/ g l-1	/ mg l-1	/ mg l-1	/ mg l-1
1	5,7	23,7 (17,8)	495	81	2153
20	5,6	23,7 (12,7)	1477	153	3341
40	5,1	20,7 (8,5)	2081	204	3856
80	5,3	17,2 (3,6)	3839	348	5201

5. Einfluss der Adsorptionstemperatur

Die Vorhydrolysen werden wie unter 1. beschrieben durchgeführt. Die Adsorption wird bei 135, 150, bzw. 175 °C unter Zugabe von 8 bzw. 20 g l^{-1} einer Aktivkohle, die durch eine BET-Oberfläche von 880 $m^2 g^{-1}$ gekennzeichnet ist, bei einer Adsorptionsdauer von 40 Minuten durchgeführt. Für die Adsorption bei 25°C wird das Vorhydrolysat nach der Phasentrennung auf 25°C abgekühlt und anschließend die Adsorption mit 20 g l^{-1} Aktivkohle (BET 880 $m^2 g^{-1}$) für 40 Minuten durchgeführt.

Während unter den gewählten Bedingungen (40 min Adsorptionszeit, 20 g l^{-1} Aktivkohle) bei 25°C knapp über 30 % des Lignins adsorbieren, kommt es bei der Verwendung des erfindungsgemäßen Verfahrens und Adsorption bei Temperaturen über 100 °C bereits zu einer Ligninadsorption von über 70 % (siehe Tabelle 4). Die gewählte Adsorptionstemperatur, spielt dabei kaum mehr eine Rolle, solange sie über 100 °C liegt. Dieses Phänomen ist dadurch zu erklären, dass bereits nach minimaler Adsorptionszeit die maximale Adsorption erreicht ist und durch die isotherme Phasentrennung das Vorhydrolysat-Aktivkohle-Gemisch für minimale Zeit 170 °C ausgesetzt ist. Siehe dazu Beispiel 4.

Tabelle 4: Temperatureinfluss der Ligninadsorption

Temperatur	Ligningehalt
/ °C	/ g l-1
25	6,9
135	2,5
150	2,3
170	2,6

6. Einfluss der BET-Oberfläche der Aktivkohle

Die Vorhydrolysen werden wie unter 1. beschrieben unter Zugabe von zwei verschiedenen Aktivkohlen bzw. einem Aktivkoks, gekennzeichnet durch BET-Oberflächen von 880, 555 bzw. 280 $m^2 g^{-1}$, bei einer Adsorptionstemperatur von 170 °C und einer Adsorptionsdauer von 20 Minuten durchgeführt. Die Ergebnisse der Nachbehandlung sind in Tabelle 5 zusammengestellt. Es ist deutlich zu erkennen, dass mit steigender BET-Oberfläche die Adsorptionsfähigkeit für Lignin, d.h. die Beladung der Aktivkohlen signifikant zunimmt. Ein Ligningehalt von etwa 3 g l^{-1} kann entweder durch 20 g l^{-1} Aktivkohle mit einer BET-Oberfläche von 880 $m^2 g^{-1}$, etwa 30 g l^{-1} Aktivkohle mit einer Oberfläche von 555 $m^2 g^{-1}$ oder aber durch über 90 g l^{-1} einer Aktivkohle mit einer BET-Oberfläche < 300 $m^2 g^{-1}$ erreicht werden. Dieses

Resultat spricht deutlich dafür, dass für die Verwendung im erfindungsgemäßen Verfahren Aktivkohlen mit BET-Oberflächen über 500 m² g^{-1}ausgewählt werden sollten.

Tabelle 5: BET-Einfluss auf die Ligninadsorption

BET-Oberfläche	Aktivkohle	Ligningehalt
/ m² g-1	/ g l-1	/ g l-1
880	8	5,6
880	20	3,0
880	48	0,4
555	24	4,1
555	36	2,1
555	48	1,8
280	48	5,5
280	96	3,4
280	144	2,1

Referenzen

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Patentansprüche:

1. Verfahren zur Gewinnung hochwertiger Produkte aus lignozellulosischem Material, insbesondere Holz, umfassend die Schritte:
    a. Vorhydrolyse des lignozellulosischen Materials,
    b. Abtrennung zumindest eines Teils des Hydrolysates vom lignozellulosischen Material,
    c. direkte Adsorption der Verkrustungsbildner aus dem Hydrolysat an einem geeigneten Adsorbens und nachfolgend
    d. Weiterverarbeitung des Hydrolysates zur Gewinnung vielfältiger Produkte, zum Beispiel aus den Oligosacchariden und Monozuckern sowie Essigsäure,

    dadurch gekennzeichnet, dass Schritt c. bei einer Temperatur des Hydrolysates von mehr als 60°C durchgeführt wird.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass die Vorhydrolyse bei einem Verhältnis von lignozellulosischem Material zu Hydrolysat in einem Bereich von 1:1 bis 1:10, bevorzugt von 1:2 bis 1:4, durchgeführt wird.

3. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass zur Vorhydrolyse ein Verfahren ausgewählt wird aus der Gruppe bestehend aus Autohydrolyse mittels Wasser als flüssige Phase, saure Hydrolyse unter Zusatz von Mineralsäuren und saure Hydrolyse unter Zusatz von organischen Säuren.

4. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass die Abtrennung des Hydrolysates durch Ablassen, durch Verdrängung durch ein Gas oder durch Verdrängung durch eine Flüssigkeit erfolgt.

5. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass die Adsorption direkt nach der Abtrennung des Hydrolysates erfolgt.

6. Verfahren gemäß Anspruch 5, dadurch gekennzeichnet, dass zwischen Abtrennung der flüssigen Phase und Adsorption das Hydrolysat eine Temperatur von 100 °C nicht unterschreitet.

7. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass die Adsorption bei Temperaturen zwischen 100 und 190 °C stattfindet, bevorzugt aber bei der Temperatur der Vorhydrolyse.

8. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass das Adsorbens ausgewählt wird aus der Gruppe von Substanzen, die selektiv Krustenbildner adsorbieren.

9. Verfahren gemäß Anspruch 8, dadurch gekennzeichnet, dass das Adsorbens Aktivkohle ist.

10. Verfahren gemäß Anspruch 9, dadurch gekennzeichnet, dass das Adsorbens Aktivkohle mit einer BET-Oberfläche > 600 $m^2 g^{-1}$ ist.

11. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass zur Weiterverarbeitung des Hydrolysates ein Verfahren aus der Gruppe bestehend aus Fermentation, enzymatischer Umsetzung und Membranprozessen ausgewählt wird.

12. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass zwischen Schritt c. und Schritt d. zunächst eine Säure zum Gemisch aus Adsorbens und Hydrolysat zugegeben wird, um die oligomeren Zucker in monomere Zucker zu hydrolysieren und anschließend das Adsorbens vom Hydrolysat abgetrennt wird

13. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, dass das vorhydrolysierte lignozellulosische Material zu Chemiezellstoff weiterverarbeitet wird.

INTERNATIONAL SEARCH REPORT

International application No
PCT/AT2011/000231

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C1/00 D21C3/00 C12P19/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21C C12P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 101 58 120 A1 (KARSTENS TIES [DE]) 18 June 2003 (2003-06-18) cited in the application -----	1-13
A	US 5 503 996 A (TORGET ROBERT W [US] ET AL) 2 April 1996 (1996-04-02) cited in the application -----	1-13
A	US 2009/218055 A1 (UUSITALO PAIVI [FI] ET AL) 3 September 2009 (2009-09-03) cited in the application -----	1-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search 17 November 2011	Date of mailing of the international search report 24/11/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Naeslund, Per

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/AT2011/000231

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 10158120 A1	18-06-2003	AU 2002358051 A1	10-06-2003
		DE 10158120 A1	18-06-2003
		EP 1448801 A1	25-08-2004
		US 2005065336 A1	24-03-2005
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		US 2009218055 A1	03-09-2009
		WO 2007090926 A1	16-08-2007

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/AT2011/000231

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
INV. D21C1/00 D21C3/00 C12P19/00
ADD.

Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
D21C C12P

Recherchierte, aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

EPO-Internal, WPI Data

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	DE 101 58 120 A1 (KARSTENS TIES [DE]) 18. Juni 2003 (2003-06-18) in der Anmeldung erwähnt -----	1-13
A	US 5 503 996 A (TORGET ROBERT W [US] ET AL) 2. April 1996 (1996-04-02) in der Anmeldung erwähnt -----	1-13
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☐ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen ☒ Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen :

"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

"E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist

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"X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann allein aufgrund dieser Veröffentlichung nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden

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"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche 17. November 2011	Absendedatum des internationalen Recherchenberichts 24/11/2011
Name und Postanschrift der Internationalen Recherchenbehörde Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bevollmächtigter Bediensteter Naeslund, Per

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
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