

## EFFECTS OF HOT WATER EXTRACTION IN A BATCH REACTOR ON THE DELIGNIFICATION OF BIRCH WOOD

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The amount of residual lignin in birch wood after a hot water extraction in a batch reactor was investigated as a function of extraction temperature and time. A kinetic model fitting the experimental data was then developed to explain delignification of wood during a hot water treatment. Results showed that delignification kinetics involves simultaneous degradation and condensation reactions, with degradation of lignin being much faster than its condensation. Native lignin in wood was successfully modeled as the sum of two fractions with different degradation rates. The rates of degradation and condensation increased along with increasing extraction temperature. The proportion of acid-soluble lignin to acid-insoluble (Klason) lignin in the wood residue decreased with increasing extraction temperature and time, probably due to chemical and structural changes in the lignin during the hot water treatment. Condensed lignin was predominantly determined as Klason lignin. On the other hand, the amount of soluble lignin in the extraction liquor increased slightly with temperature, but remained mostly constant after any extraction time. An insoluble fraction in the liquor that originated from precipitated lignin fragments is believed to contain traces of degradation products from carbohydrates or other degradation compounds.

*Keywords:* Autohydrolysis; Birch; Delignification kinetics; Hot water extraction; Lignin condensation; Wood fractionation

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### INTRODUCTION

The concept of a wood biorefinery is envisioned as the selective separation of the three main wood components, cellulose, hemicelluloses and lignin, for the production of high value-added products (Ragauskas et al. 2006; van Heiningen 2006). Within this context, the use of hot water treatments for extracting and recovering the hemicelluloses from wood has gained much attention in recent years, mainly because pure water is the only solvent used (Garrote et al. 1999; Song et al. 2008; Tunc and van Heiningen 2008; Yu et al. 2008). At an industrial scale, water extractions are solely utilized in the form of steam in prehydrolysis-kraft processes (PHK) for the production of dissolving pulps (Sixta 2006; Springer and Harris 1982). Hot water treatments with bulk water are not applied commercially due to several problems related to the processability of the hydrolysate (Leschinsky et al. 2008). The wood residue after the extraction, composed mostly of cellulose and lignin, can be further subjected to pulping for the production of hemi-lean pulps, using lesser chemicals and shorter pulping times than in the case of

untreated wood (Garrote et al. 2003; Kubikova et al. 1996; Reguant et al. 1997; Yoon and van Heiningen 2008).

Hot water extractions, also called autohydrolysis, have been generally applied to hardwoods. Their higher amount of acetyl groups linked to the hemicelluloses and a good delignification efficiency, with lesser tendency for lignin condensation, make hardwood species more suitable to water extraction than softwoods (Sixta 2006). The extraction temperatures often range between 130 °C and 240 °C. Up to 180 °C, hot water treatments are suggested for conventional prehydrolysis and for recovering the extracted sugars, dissolved in the hydrolysate. Above 180 °C, hot water treatments are used for selective biomass fractionation (Mok and Antal Jr. 1992). The particle size of the raw wood material varies from industrial-size chips to fine wood meal. In general, due to mass and heat transfer limitations, the larger the particle size, the lower is the yield of extracted products. The total amount of dissolved solids after a hot water extraction of spruce wood has been reported to decrease by 60% when wood chips are used instead of ground wood meal (Song et al. 2008). The degree of extraction may also depend on the liquid-to-wood ratio of the process, owing to solubility limitations (Chen et al. 2010).

The degradation of wood components during a hot water treatment proceeds via hydronium-catalyzed reactions. Hydronium ions generated by water autoionization cleave the acetyl groups linked to the hemicelluloses, with the consequent formation of acetic acid (Garrote et al. 1999, 2001). In such acidic conditions, lignin depolymerization occurs predominantly through homolytic cleavage of  $\alpha$ -O-4 and  $\beta$ -O-4 bonds (Bobleter 1994; Leschinsky et al. 2008; Li et al. 2000; Meshgini and Sarkanen 1989). These bonds are the most abundant in lignin structures of both hardwoods and softwoods, with a relative frequency of 5 to 10% and 40 to 60%, respectively (Alén 2000). The rate of cleavage of  $\alpha$ -aryl ether bonds under acidic conditions has been reported to be 100 times faster than that of  $\beta$ -O-4 bonds (Meshgini and Sarkanen 1989). Depolymerization reactions, however, are followed by the condensation of lignin fragments already dissolved in the liquor. Condensation reactions occur as the carbonium ion in the intermediate, formed through the scission of the aryl ether bond, reacts by radical coupling with another electron-rich carbon, forming stable carbon-carbon linkages (Li and Gellerstedt 2008; Li et al. 2000). The condensed lignin precipitates onto the fibers, thus increasing the amount of residual lignin in wood. Both degradation and condensation reactions appear to be favored by elevated temperatures (Bobleter 1994; Lora and Wayman 1978).

Some of the lignin fragments solubilized in the extraction liquor, particularly those of high molecular weight, may condense during cooling, forming dark and sticky precipitates (Leschinsky et al. 2008, 2009b). The formation of such precipitates makes the handling of extraction liquors difficult and causes operational problems in the digesters and tank farms. The lignin solubilized in the extraction liquor and the lignin that precipitates have been proposed to originate largely from the acid-soluble and acid-insoluble (Klason) lignin in wood, respectively (Leschinsky et al. 2009a).

As already mentioned, a hot water treatment involves at least consecutive depolymerization and condensation reactions in lignin. The maximum amount of lignin removed by a hot water treatment shifts to shorter reaction times with increasing temperature (Bobleter 1994; Lora and Wayman 1978). In addition to partial

delignification, hot water extractions appear to increase the reactivity of the lignin remaining in the wood residue. This activation of lignin improves its removal in a subsequent delignification process (El Hage et al. 2010; Lora and Wayman 1978; Reguant et al. 1997). More than 90% of the original lignin in aspen wood meal was removed by a 9:1 dioxane:water extraction following a hot water treatment at 215 °C for 4 minutes (Lora and Wayman 1978). However, condensation of lignin during the hot water treatment results in increased resistance to delignification in a subsequent pulping process (El Hage et al. 2010; Lora and Wayman 1978).

Hot water treatments at elevated temperatures (above 180 °C) may be used to remove and activate the lignin in wood prior to pulping. Under such conditions the hot water treatment may remove quantitatively the hemicelluloses while preserving the cellulose. The suitability of such an intense hot water treatment for the production of dissolving pulps as well as for the recovery of sugars in high yield will be further investigated. An appropriate pulping method should then be applied to maximize the cellulose yield. Excessive condensation of lignin during the hot water extraction should also be avoided if a high degree of delignification at the lowest cost is to be accomplished.

Information on delignification kinetics of wood during a hot water treatment is rather scarce in the literature. Such information may be of importance for optimizing hot water extractions as a pretreatment prior to subsequent pulping. The purpose of this study was to determine the amount of residual lignin in birch wood after a hot water treatment in a batch reactor under different process conditions. Then, a model fitting the experimental data is proposed for explaining delignification kinetics of wood during a hot water extraction. Furthermore, the effects of a hot water treatment on the formation and the recovery of separate lignin fractions in both the wood residue and the extraction liquor are discussed.

## EXPERIMENTAL

### Wood Material

Coarse sawdust from silver birch (*Betula pendula*) wood felled in Southern Finland was air-dried at room conditions and ground in a Wiley mill to a particle size between -30 mesh and +60 mesh (0.6 mm - 0.25 mm). The chemical composition of the wood meal is listed in Table 1. The ground wood meal was extracted with acetone for 6 hours in a Soxhlet apparatus. Extractives-free wood meal was then air-dried, and the dry matter content was determined by oven-drying representative samples in a convection oven at 105 °C overnight.

### Hot Water Extractions

Hot water extractions were conducted in a batch reactor of 300 mL volume (Autoclave Engineers), equipped with temperature control, a pressure gauge, a mechanical stirrer, and a valve for the removal of extraction liquor. About 5 grams (oven-dry mass) of extractives-free wood meal were placed in the reactor along with 200 mL of deionized water, reaching a liquid-to-wood ratio of 40:1 g/g. Such a high liquid-to-wood

ratio was selected to minimize any limitations on the solubility of extracted wood components. After sealing the reactor and purging it with nitrogen, the reactor was heated up to a predetermined setup temperature. Once the setup temperature was reached, an isothermal treatment followed. At the end of the isothermal stage, the extraction liquor was removed from the reactor and collected. The reactor was then rapidly cooled by circulating cold water around it. The wood residue was recovered from the reactor, washed with warm water, and air-dried. The wood yield was determined on a dry mass basis after oven-drying representative samples at 105 °C overnight. The experimental parameters for the hot water extractions are shown in Table 2.

**Table 1.** Chemical Composition of Birch Wood Meal

Component	Amount (% on oven-dry mass)
Rhamnose	0.10
Galactose	0.67
Mannose	1.76
Xylose	20.93
Glucose	43.05
Klason lignin	17.70
Acid-soluble lignin	4.66
Acetyl groups	3.54
Extractives	1.72
Others	5.87

\* Calculated as anhydrosugars

\*\* Calculated by difference

**Table 2.** Experimental Parameters for the Hot Water Treatments

Setup temperature (°C)	Isothermal treatment (min)	Wood yield (%)	pH values
180	0 – 180	91.0 – 58.4	4.1 – 3.2
200	0 – 180	60.7 – 50.4	3.4 – 2.9
220	0 – 60	53.6 – 44.0	3.5 – 2.8
240	0 - 30	47.2 – 33.9	3.4 – 2.7

A black precipitate was found to form inside the cooling coil as the extraction liquor was removed from the reactor, particularly at temperatures above 200 °C. In order to recover it, about 100 mL of hot water was circulated through the cooling coil after each hot water extraction trial. This washing water was collected and combined with the extraction liquor. The insoluble fraction in the combined liquor was recovered by conducting two consecutive centrifugations at about 8,000 rpm. for 30 min each. The supernatant was then combined with the washing filtrate from the wood residue. The experimental flow-scheme is illustrated in Fig. 1.

### Analytical Determinations

The wood residue was subjected to the same type of analyses as the extractives-free wood meal before the hot water extractions. The carbohydrates, acetyl groups, Klason lignin, and acid-soluble lignin were determined according to the analytical method (NREL/TP-510-42618) issued by the U.S. National Renewable Energy Laboratory (NREL). The carbohydrates were determined by High Performance Anion

Exchange Chromatography with Pulse Amperometric Detection (HPAEC-PAD) in a Dionex ICS-3000 column. The acetyl content was determined by High Performance Liquid Chromatography (HPLC) in a Dionex Ultimate 3000 column. The acid-soluble lignin was determined in a Shimadzu UV-2550 spectrophotometer at a wavelength of 205 nm. The soluble lignin in the liquor was determined as in the case of acid-soluble lignin in wood. The insoluble fraction in the liquor was determined gravimetrically after centrifuging and air-drying.

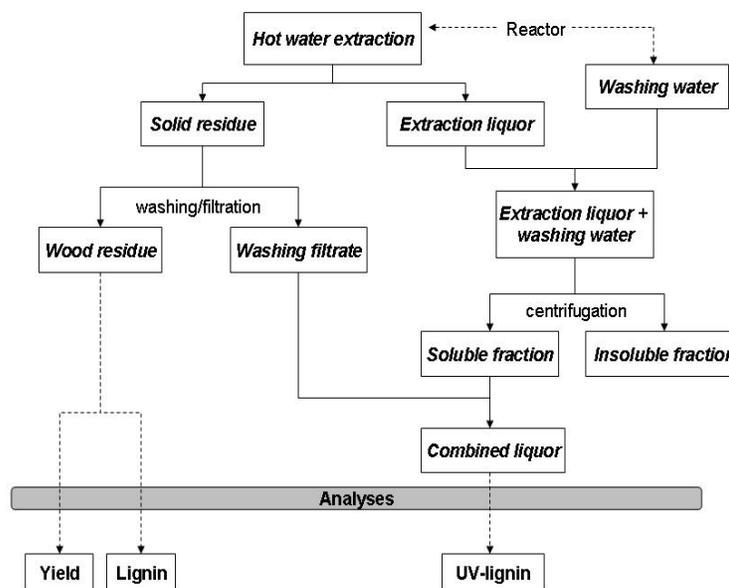


Fig. 1. Experimental flow-scheme of the hot water extractions and analyses

### Time-Temperature Correction

In processes where the heating up phase is long in relation to the isothermal treatment at the setup temperature, the degradation of wood components during the preheating cannot be avoided. In order to account for any degradation of lignin during the heating up phase, the heating up time (about 15 min) was converted into isothermal reaction time by Eq. 1,

$$t_{T_S} = \sum_{T=30}^{T_S} t_T \cdot \frac{k_T}{k_{T_S}} \quad (1)$$

where  $t_{T_S}$  (min) and  $k_{T_S}$  ( $\text{min}^{-1}$ ) are the converted isothermal time and the delignification rate at the setup temperature, respectively, and  $t_T$  (min) and  $k_T$  ( $\text{min}^{-1}$ ) are the time and the delignification rate at any temperature during the heating up phase. By assuming the same activation energy between the initial temperature and the setup temperature, the delignification rate at any temperature during the preheating was approximated by an Arrhenius expression as,

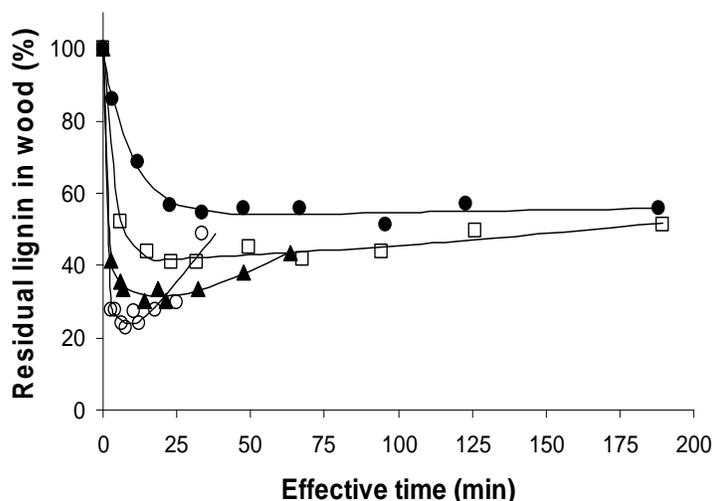
$$k_T = k_{T_S} \cdot \exp\left(\frac{-E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_S}\right)\right) \quad (2)$$

where  $E_a$  ( $\text{J}\cdot\text{mol}^{-1}$ ) is the activation energy,  $R$  is the universal gas constant ( $8.31 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$ ),  $T$  (K) is any temperature during the preheating, and  $T_S$  (K) is the setup temperature. The converted isothermal time from the heating up phase determined in Eq. 1 was then added to the actual isothermal time of the reaction, resulting in an effective reaction time for any hot water extraction.

## RESULTS AND DISCUSSION

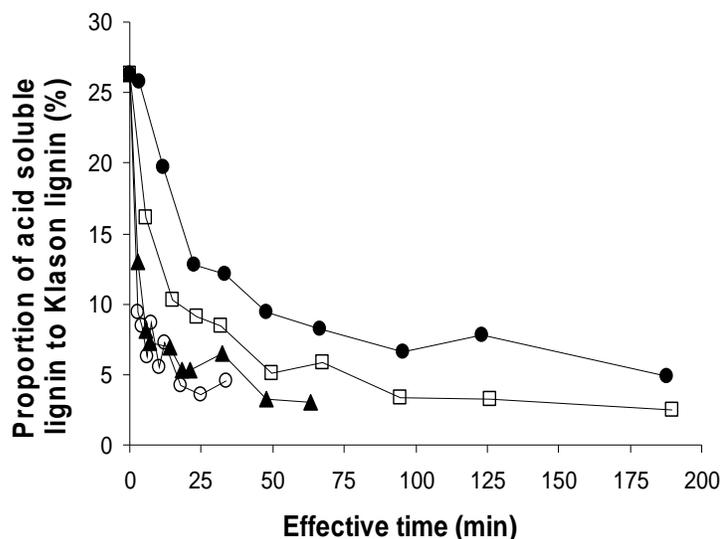
### Residual Lignin in Wood

The amount of residual lignin in wood after a hot water extraction was investigated as a function of treatment intensity. Residual lignin decreased with increasing extraction temperature and time, however reaching a minimum value that was characteristic for each temperature (Fig. 2). Thereafter, extending extraction time resulted in an increasing amount of residual lignin. Degradation of lignin under the acidic conditions generated during a hot water treatment involves the cleavage of  $\alpha$ - and  $\beta$ -aryl ether bonds (Bobleter 1994; Leschinsky et al. 2008; Meshgini and Sarkanen 1989). The carbonium ion in the resulting intermediate can then react with an electron-rich carbon to form stable carbon-carbon linkages, leading to condensation of lignin (Li and Gellerstedt 2008; Li et al. 2000). The occurrence of condensation reactions explains the increase in residual lignin as shown in Fig. 2. The condensation of lignin was clearly most pronounced at high temperatures. A hot water extraction at  $240^\circ\text{C}$  and a few minutes of reaction time was able to remove nearly 80% of the original lignin in birch wood.



**Fig. 2.** Residual lignin in wood as a function of effective reaction time. *Filled circles*, temperature  $180^\circ\text{C}$ ; *empty squares*, temperature  $200^\circ\text{C}$ ; *filled triangles*, temperature  $220^\circ\text{C}$ ; *empty circles*, temperature  $240^\circ\text{C}$ . Data points correspond to experimental observations. Lines correspond to a proposed kinetic model for delignification.

Residual lignin in wood was determined as the sum of Klason lignin and acid-soluble lignin. It is well known that the lignin content, particularly in hardwoods, cannot be fully quantified by the Klason method because a part of the lignin remains soluble in the acidic filtrate. Acid-soluble lignin is largely composed of low-molecular weight compounds that originate from degradation of lignin (Yasuda et al. 2001). The proportion of acid-soluble lignin to Klason lignin in the wood residue decreased rapidly at first with increasing treatment intensity, and then the decrease was reduced (Fig. 3). Considering the occurrence of condensation reactions in the lignin during a hot water extraction, the decreasing proportion of acid-soluble lignin to Klason lignin may indicate changes in the structure and/or in the chemical composition of lignin. This is likely to affect its reactivity in subsequent delignification processes.

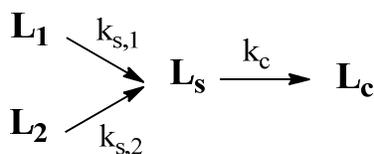


**Fig. 3.** Proportion of acid-soluble lignin to Klason lignin in the wood residue as a function of effective reaction time. Symbols are the same as in Fig. 2.

### Delignification Kinetics

Native lignin in wood has previously been modeled as the sum of two separate fractions with different degradation rates, forming a sole lignin product once solubilized (Vega and Bao 1992). The presence of two forms of lignin in wood might be explained in relation to the type of carbohydrates to which lignin is attached. Glucomannan- and xylan-lignin complexes have been found to be dominant in spruce wood, with each of these complexes exhibiting different chemical structure and different degradation rates during kraft pulping (Lawoko et al. 2004, 2005). A third form of lignin attached to glucan has also been found, although its relative amount in spruce wood is minor in comparison to the glucomannan- and xylan-lignin complexes (Lawoko et al. 2004, 2005). Alternatively, the assumption of two separate lignin fractions in wood might be related to the different reactivity of the  $\alpha$ - and  $\beta$ -ether bonds. It has been reported that the rate of hydrolysis of  $\alpha$ -ether bonds in acidic conditions is about two orders of magnitude faster than that of  $\beta$ -ether bonds (Meshgini and Sarkanen 1989).

Delignification kinetics of birch wood during a hot water extraction was assumed to proceed as,



where  $L_1$  and  $L_2$  are easy and hard to remove lignin fractions, respectively. At  $t = 0$ ,  $L_1 + L_2 = 1$ , and  $L_s + L_c = 0$ . If degradation and condensation of lignin follow a first-order reaction, then the above reaction scheme can be expressed as,

$$\frac{dL_1}{dt} = -k_{s1}L_1 \quad (3)$$

$$\frac{dL_2}{dt} = -k_{s2}L_2 \quad (4)$$

$$\frac{dL_s}{dt} = k_{s1}L_1 + k_{s2}L_2 - k_cL_s \quad (5)$$

$$\frac{dL_c}{dt} = k_cL_s \quad (6)$$

where  $k_{s1}$  and  $k_{s2}$  are the degradation rates for the easy and hard to remove lignin, respectively,  $k_c$  is the condensation rate for the lignin solubilized in the extraction liquor, and  $t$  is the effective reaction time.

The system of differential equations was solved analytically by obtaining expressions for the amounts of various types of lignin ( $L_1$ ,  $L_2$ ,  $L_s$ , and  $L_c$ ) as a function of time, with the kinetic coefficients  $k_1$ ,  $k_2$ ,  $k_s$ ,  $k_c$  and the initial amounts of  $L_1$  and  $L_2$  as parameters. In the model, the measured amount of lignin in the wood residue corresponds to the sum of  $L_1$ ,  $L_2$ , and  $L_c$ , and thus the analytic expression of this sum was fitted to the measurement data. Each extraction temperature was treated separately. The fits were performed using the NonlinearFit-function of Mathematica 5.2.

The proposed kinetic model fitted well to the experimental data, as shown in Fig. 2. Therefore, delignification kinetics during a hot water extraction can be modeled in terms of simultaneous degradation (solubilization) and condensation reactions, with lignin in wood being the sum of two separate fractions with different degradation rates. It is worth noting, however, that changes in the liquid-to-wood ratio of the extraction process may affect delignification kinetics owing to solubility limitations.

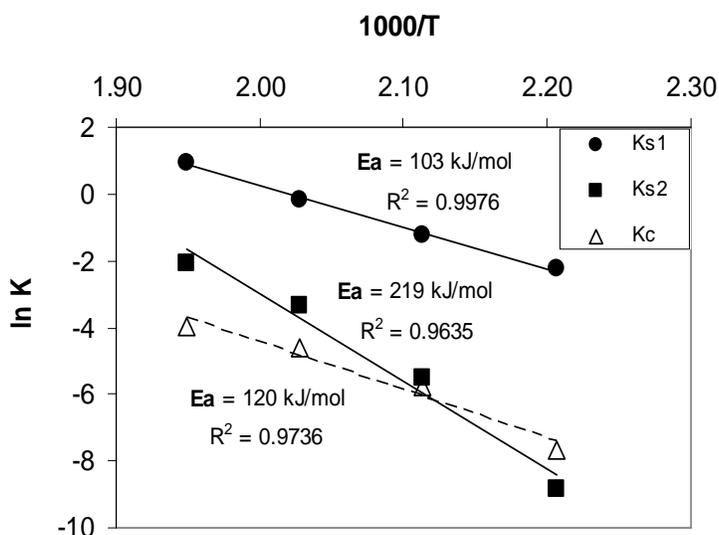
The kinetic parameters, determined from equations 3 to 6 and listed in Table 3, indicate that degradation and condensation reaction rates increased with temperature. At any temperature, degradation of lignin proceeded faster than its condensation. The proportion of  $L_1$  increased from 46% to 63% along with increasing temperature, while the proportion of  $L_2$  obviously decreased. Considering that  $\alpha$ - and  $\beta$ -ether bonds represent about 5 to 10% and 40 to 60%, respectively, of the linkages in wood lignin (Alén 2000), it is unlikely that the two forms of lignin in wood are related to these types of bonds. The assumption of lignin attached to different carbohydrates having different degradation rates might seem more plausible. Nonetheless, reasons for the changes in the proportion

of lignin fractions with increasing temperature are unknown and subject for further investigations.

**Table 3.** Kinetic Parameters for the Delignification of Birch Wood Meal

Temperature (°C)	$K_{s1}$ ( $\text{min}^{-1}$ )	$K_{s2}$ ( $\text{min}^{-1}$ )	$K_c$ ( $\text{min}^{-1}$ )	L1 (%)	L2 (%)
180	0.10498	0.00014	0.00046	46.39	53.61
200	0.29380	0.00398	0.00319	58.25	41.75
220	0.85814	0.03595	0.00995	61.41	38.59
240	2.53846	0.12786	0.01917	63.26	36.74

Based on the reaction rates in Table 3, the activation energies of degradation and condensation were determined through an Arrhenius plot (Fig. 4). The activation energy for the degradation of  $L_1$  (103 kJ/mol) was somewhat higher than the activation energy for autocatalyzed delignification of eucalyptus wood (78.2 kJ/mol) reported by Vázquez et al. (1995). The removal of  $L_2$  was very dependent on temperature, with an activation energy of 219 kJ/mol. The activation energy for the degradation of  $L_1$  was used for determining the delignification rate at any temperature during the preheating (Eq. 2). On the other hand, the activation energy for lignin condensation was 120 kJ/mol, which is a typical value for chemically controlled reactions. The temperature dependence of the different reaction rates is illustrated by a decreasing  $k_{s1}/k_c$  ratio with increasing temperature, while at the same time the  $k_{s2}/k_c$  ratio is significantly increasing. This indicates that the degradation of the resistant lignin fraction ( $L_2$ ) in wood continues with rising temperature, while the easily removable lignin ( $L_1$ ) increasingly undergoes condensation.

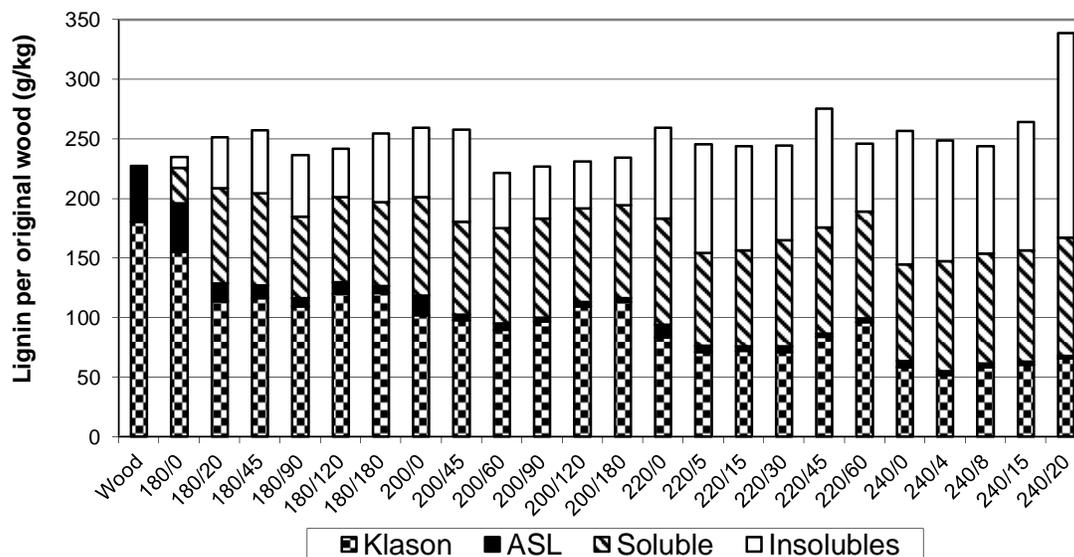


**Fig. 4.** Arrhenius plot showing the values of activation energy for degradation and condensation reactions in birch wood lignin

### Mass Balances of Lignin

The mass balance of the different lignin fractions determined after the hot water treatment is plotted in Fig. 5. It should be noted that some experiments were not followed by subsequent washing of the reactor, and thus the black precipitate formed inside the

reactor system could not be recovered. Because this black precipitate accounted for a significant part of the total insoluble fraction, those particular experiments were not included in the mass balances.



**Fig. 5.** Mass balance of lignin for the hot water extractions. The first part in the sample name in the x-axis corresponds to the extraction temperature, and the second part corresponds to the isothermal reaction time. Klason and acid-soluble lignin (ASL) were determined from the wood residue, while soluble and insoluble fractions were determined from the hydrolysate

At any temperature, the amount of Klason lignin in the wood residue increased after extended extraction times (Fig. 5). A similar observation was reported by Leschinsky et al. (2009a). Because the proportion of acid-soluble lignin to Klason lignin decreased with increasing treatment intensity (Fig. 3), it can be concluded that condensed lignin is predominantly determined as Klason lignin.

From the lignin that solubilized into the liquor during the hot water extraction, some of it remained soluble after the extraction process, while some precipitated during cooling, forming an insoluble fraction. The amount of soluble lignin in the extraction liquor increased, from 75 to 92 g per kg of original dry wood, with increasing extraction temperature from 180 °C to 240 °C (Fig. 5). At any temperature, however, the amount of soluble lignin in the liquor remained mostly constant after any extraction time. Again, this in line with previous results by Leschinsky et al. (2009a), reporting similar amounts of soluble lignin (32 to 36 g per kg of original dry wood) after various extraction intensities at 170 °C. Those authors reported that the soluble lignin in the liquor was likely to correspond to the amount of acid-soluble lignin dissolved from the wood residue. Obviously, this was not the case in the present study, as the amount of soluble lignin in the liquor after the extractions (75 to 92 g per kg of original dry wood) was much higher than the amount of acid-soluble lignin in native wood (about 47 g per kg of original dry wood).

The insoluble fraction recovered by centrifugation was assumed to originate completely from lignin, and thus it was considered as such for the mass balance. The

reason for such assumption was that previous studies have reported that these insoluble products contain mostly condensed structures from solubilized lignin fragments, especially from those of higher molecular mass (Leschinsky et al. 2008; 2009b). In general, a somewhat higher amount of lignin was observed in the mass balances of extracted wood as compared to untreated wood, and in particular after a treatment at 240 °C for 20 min (Fig. 5). This is likely due to degradation products from carbohydrates or other degradation compounds being attached to condensed lignin fragments in the insoluble fraction (Overend and Chornet 1987). The association of degradation compounds to the insoluble fraction appeared to be most pronounced at high treatment intensities. Furthermore, the insoluble fraction was determined gravimetrically after air-drying, and thus it may have contained some moisture. This probably resulted in a slight excess in the mass of precipitates measured.

## CONCLUSIONS

1. Significant delignification of birch wood was accomplished by a hot water extraction alone. Nearly 80% of native lignin in birch was solubilized after a hot water extraction at 240 °C and a few minutes of reaction time, before excessive condensation prevailed.
2. Delignification kinetics of wood during a hot water treatment was successfully modeled by simultaneous degradation (solubilization) and condensation reactions in lignin. The rates of degradation and condensation increased with temperature, and at any temperature, the degradation rate of lignin was much faster than condensation.
3. Native lignin was modeled as the sum of two fractions with different degradation rates. This might be related to different lignin-carbohydrates complexes within the cell wall having different degradation rates. The easily solubilized lignin fraction increased with temperature, while the lignin fraction that was harder to solubilize obviously decreased.
4. The proportion of acid-soluble lignin to Klason lignin in the wood residue decreased with increasing extraction temperature and time. This probably indicates structural and/or chemical changes in lignin induced by condensation reactions during the hot water extraction, which may affect lignin reactivity in subsequent delignification processes.
5. The amount of Klason lignin in the wood residue increased after extended extraction times. Condensed lignin in the wood residue was predominantly determined as Klason lignin.
6. The amount of soluble lignin in the liquor increased slightly with increasing extraction temperature from 180 °C to 240 °C. At any temperature, however, the amount of soluble lignin in the liquor remained mostly constant after any extraction time.
7. An insoluble fraction was recovered from the liquor. Based on the mass balances of lignin, this insoluble fraction appears to originate mostly from lignin, although other degradation compounds are likely to be attached. This resulted in a somewhat higher amount of total lignin in the mass balance of extracted wood, particularly at high treatment intensities.

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