

PUBLICATION I

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Part 1. Results from direct analyses

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Lignin oxidation mechanisms under oxygen delignification conditions. Part 1. Results from direct analyses

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Abstract

Oxidation of softwood and hardwood kraft lignins was observed under conditions of oxygen delignification (90°C and 110°C; 0.6 and 0.9 MPa) as a function of time by means of a number of analysis techniques and quantitative information was obtained on the degradation and formation of various compounds and structures. The decrease in reactor pressure was monitored during a 4-h reaction period. During the first 60 min, lignin reactivity was high, while a very intense stage took place during the first 20 min. The reactions decelerated after the first 60 min and after 120 min the reactions did not significantly advance. The oxygen consumption after 4-h reaction was 1.3–1.5 mole O₂ per 1 mole lignin depending on the conditions. In the first 20 min, 50%–60% of the oxygen was consumed and the consumption increased only slightly after 60 min. At 90°C, the changes in all observed quantities were smaller throughout the whole 4-h reaction period than at 110°C. Under the studied conditions, increasing the reaction temperature, rather than the pressure, had primary significance in the increasing rate of lignin degradation. Hardwood kraft lignin was more reactive than softwood kraft lignin. The results obtained in this study are the basis for the development of a mechanistic model for the oxygen delignification process of pulps to be published in subsequent papers.

Keywords: kraft lignin; lignin; modeling; oxidation; oxygen; oxygen consumption.

Introduction

Lignin, a three-dimensional amorphous polymer consisting of methoxylated phenylpropane structures, is one of the three essential components of wood together with cellulose and hemicelluloses, which form a special supramolecular architecture (Sarkanen and Ludwig 1971; Salmén and Burgert 2008). In chemical pulping processes, lignin is removed from

wood and the fibers are separated from each other. About 92%–94% of the fiber lignin can be removed by kraft cooking with reasonable selectivity (Gellerstedt and Lindfors 1991). The residual lignin is removed during the subsequent delignification and bleaching stages, typically starting by oxygen in alkaline medium. During this oxygen stage (O), the degree of delignification increases, depending on the operation parameters, in the range of 35%–50% (Sjöström 1993; Alén 2000; van Heiningen et al. 2003). The average oxygen consumption in industrial oxygen delignification is 0.14% per kappa number for softwoods (SW) and 0.16% for hardwoods (HW) (McDonough 1996).

In oxygen delignification, the most reactive sites in lignin are the phenolic structures, more specifically their phenolate forms in the alkaline solution. Thus, oxidation rate at a given temperature should be controlled by the content of phenolic units, pH, and concentration of oxygen. In the residual lignin of kraft pulp, 25%–40% of the aromatic structures have been reported to be phenolic (Gellerstedt and Lindfors 1984; Lindgren and Lindström 1996; Jiang and Argyropoulos 1999; Moe and Ragauskas 1999). Delignification occurs fast at the beginning of the oxygen stage and decelerates after reaching the 50% reduction level (Lai et al. 1994). The amount of phenolic hydroxyls decreases and the amount of carboxylic acids increases in the O stage (Gellerstedt and Lindfors 1987; Sun and Argyropoulos 1995; Jiang and Argyropoulos 1999; Moe and Ragauskas 1999). Residual lignin isolated from SW kraft pulp (*Picea mariana*, kappa no. 30.9) was oxygen treated by Asgari and Argyropoulos (1998) at elevated temperatures. The quoted authors found that the rate of reduction of phenolic guaiacyl units is considerably slower at 80 and 95°C than at or above 110°C. Furthermore, the degradation of guaiacyl units at temperatures above 100°C proceeds in two distinct phases: an initial rapid decrease observed within 20–40 min is followed by a significantly slower regime.

The changes observed in lignin structure can be explained by the following reaction mechanism. The phenolates react with oxygen: phenoxyl radical is the primary oxidation product and superoxide (radical anion) is the one-electron reduction product of oxygen (Gierer et al. 2001). In secondary reactions, the phenoxyl radicals react with superoxide or oxygen forming quinone and muconic acid type structures (Gierer 1997). Superoxide also undergoes dismutation to oxygen and hydrogen peroxide and hydroxyl radicals are formed via further decomposition reactions. Hydrogen peroxide oxidizes the quinone intermediates further. In the aromatic ring-opening reaction and following hydrolysis, methanol is released from the methoxy group attached to C-3 and/or C-5. The dissociated form of the hydroxyl radical (oxyl anion radical) reacts with the side chain of lignin form-

ing aliphatic acids and α -carbonyl structures (Gierer 1990; Sjöström 1991; Gavrilescu 2005). In summary, all the complex oxidation reactions cause lignin depolymerization and introduce acidic groups in lignin and consequently enhance its dissolution. Oxygen is also consumed in further reactions of the degradation products.

Although oxidation proceeds via ionized phenolic units, only 30%–60% of the phenolic structures are reported to react in oxygen delignification of pulps (Gellerstedt and Lindfors 1991; Sun and Argyropoulos 1995; Moe and Ragauskas 1999; Argyropoulos and Liu 2000; Akim et al. 2001). This was also observed in oxidizing experiments with isolated residual kraft lignin (Asgari and Argyropoulos 1998). One reason for the limited oxidation is the presence of condensed units (e.g., biphenyl units), which are native in wood but which can also be formed during cooking (e.g., diphenylmethane) (Lai et al. 1994; Jiang and Argyropoulos 1999; Argyropoulos and Liu 2000). Such units are fairly stable towards oxidation and are thus enriched in the residual lignin (Hortling et al. 1992; Lai et al. 1994; Argyropoulos and Liu 2000; Akim et al. 2001). The proportion of the condensed phenolic units in SW residual lignin is higher than that in HW residual lignin. The reduction of these structures can be improved by increasing the oxygen partial pressure, and the effect is greater in HW than SW lignin (Sun and Argyropoulos 1995). Syringyl (S) units are believed to be more reactive under conditions of oxygen delignification than guaiacyl (G) units. Yang et al. (2002) suggested that the bleachability of HW kraft pulp with low kappa number is detrimentally influenced by the accumulation of inert G units. Stilbene structures, existing initially in lignin and surviving the cooking, are among the most reactive structures in oxygen delignification (Ljunggren and Johansson 1990; Gellerstedt and Lindfors 1991). In addition to stilbenes, enolether structures are also formed during cooking. The content of enolethers decreases in the O stage, whereas α -carbonyl type conjugated structures are formed (Tamminen and Hortling 2001).

The objective of the present study was to provide detailed information on alkaline oxygen oxidation of SW and HW lignins for the development of a mechanistic model for the pulp oxygen delignification process. Detailed data in this regard are not provided in the literature, even if lignin reactions during oxygen delignification have been studied extensively. Therefore, experiments were performed by applying delignification conditions for the treatment of lignin, without the interference of carbohydrates or extractives. Kraft lignins isolated from black liquors were selected as starting materials, because of the large amounts of lignins needed for the experiments, which could not be isolated from pulp residual lignins. The structures of the dissolved and residual lignin are supposed to be rather similar (Akim et al. 2001; Fu et al. 2005), even though the structural changes induced by cooking are more pronounced in the dissolved lignin. For example, the content of phenolic hydroxyls in dissolved lignin has been measured to be ca. twofold greater than that in residual lignin (Gellerstedt and Lindfors 1984; Robert et al. 1984). Residual lignin composition in the modeling was

based on that reported in literature, although its reactions were based on the data obtained from the kraft lignin experiments.

This paper presents the results from the direct analyses of the kraft lignin oxidation experiments. In order to follow the reaction kinetics and determine the relative importance of different reaction routes for the kinetic model, it was necessary to quantify the degradation products in addition to the detection of structural changes in the polymeric lignin. Therefore, the oxidized lignin samples obtained from this study were further characterized by advanced analysis methods to distinguish carboxylic acids bound to lignin macromolecule and those bound to aliphatic acids.

Materials and methods

Experimental

Indulin AT, a softwood kraft lignin (KL_{SW}) and PC1369, a hardwood kraft lignin (KL_{HW}) obtained from MeadWestvaco Corp. (Appomattox, VA, USA) were dissolved in 0.1 M NaOH solution in concentration of 7.5 g l⁻¹ corresponding to the content of fiber-bound lignin in the oxygen delignification of high kappa number pulp (ca. $\kappa = 50$) at 10% consistency.

Reactor: 1-l stainless steel high-pressure batch reactor (Parr Instrumental Co., Moline, IL, USA), which was equipped with baffles and a six-bladed turbine-type impeller stirrer, an electric heating jacket, a gas inlet, a liquid sampling tube, and a gas release valve. Parameters: two temperatures (90 and 110°C) and two initial oxygen pressures (0.6 and 0.9 MPa); for operating conditions see Table 1. The preheating was continued for 30 or 90 min to reach the desired temperature. In the experiments at 110°C, the reactor was flushed with nitrogen for air before raising the temperature above 90°C. After preheating, pure oxygen was introduced in the reactor and this was set as the starting point of the oxidation reaction. In all experiments, the volume of the reaction solution was 0.8 l and the impeller was operated at 600 rpm.

Liquid samples of 50 ml were taken periodically during the whole 4-h reaction time (5, 10, 20, 30, 60, 120, 180 and 240 min after the starting point). The stirring was stopped during the sampling to avoid foaming. As the sampling lowered the reactor pressure, immediately after taking the sample more oxygen was fed to the reactor to recuperate the previous pressure. Pressure and temperature in the reactor were recorded during the whole reaction period. The pH of the samples was measured at room temperature. The preparation of both KL_{SW} and KL_{HW} solutions and preheating were repeated in separate experiments for obtaining the first samples (0 min) of the oxidation experiments. The procedure corresponded to the handling

Table 1 Experimental set-up for oxidation of kraft lignins from softwood (KL_{SW}) and hardwood (KL_{HW}).

Exp. #	Kraft lignin	Initial pressure (MPa)	Temp. (°C)	Code
1	SW	0.94	90	0.9 MPa, 90°C, SW
2	SW	0.94	110	0.9 MPa, 110°C, SW
3	SW	0.64	90	0.6 MPa, 90°C, SW
4	SW	0.64	110	0.6 MPa, 110°C, SW
5	HW	0.64	90	0.6 MPa, 90°C, HW

of the actual reaction conditions right before pressuring the reactor. The rate of oxygen dissolution in 0.1 M NaOH solution was investigated in a separate experiment (90°C, 0.6 MPa, without lignin). Furthermore, the formation/presence of hydrogen peroxide in the oxidation mixture was investigated separately (90°C, 0.6 MPa, KL_{SW}). Samples were taken as a function of time and iodometric titration of hydrogen peroxide was performed right after the sampling.

Analytical methods

Both starting lignins were analyzed for metals and sulfur. For the analysis, 0.3 g of sample was liquefied by concentrated acids (6 ml HNO₃, 2 ml H₂O₂, 1 ml HF) for 28 min in a closed vessel in a microwave oven. After dilution, Na and K were analyzed with FAAS and Ba, Ca, Cu, Fe, Mg, Mn, S, V, and Zn were analyzed with ICP-AES. The elemental analysis (C, H, S, O) and the determination of methoxyl content were conducted at Lindlar Analytische Laboratorien, Germany.

The treatment solutions as such were analyzed for several quantities. Total charge giving the sum of all acids in the solution was measured by titration. In the titration the conductivity of the sample was registered as a function of titrate addition (both 0.1 M HCl and 0.1 M NaOH; pH range 2.5–11.5). The total charge of the sample was calculated using the time difference between the equivalent points of acid and base titration curve. The method is a slight modification of the method described by Zakis (1994a). Ionization difference ultraviolet spectroscopy was used to obtain information on the amount of phenolic lignin and conjugated phenols (Zakis 1994b; Tamminen and Hortling 1999). The UV-Vis measurements were performed in alkaline (0.1 M NaOH) and near neutral conditions (pH 6) with a Perkin Elmer Lambda 900 spectrometer (Perkin Elmer, Waltham, MA, USA). Change of the aromatic lignin content during oxidation was followed as UV-lignin at 280 nm based on absorptivity values of 22.4 l g⁻¹ cm⁻¹ for SW and 22.2 l g⁻¹ cm⁻¹ for HW kraft lignin (absorptivities determined in the initial concentration). Also, lignin color was followed by measuring the absorbance at 457 nm and 280 nm (A₄₅₇/A₂₈₀) at pH 6. The degree of demethylation was followed by detecting the methanol liberated to the liquid phase by a static headspace-GC/FID method by means of Tekmar 7000 (Teledyne Tekmar, Mason, OH, USA) and HP5890 Series II devices (Hewlett-Packard Co., Palo Alto, CA, USA). Headspace method was conducted in conditions of 60°C and 25 min. Methanol concentrations were calculated in relation to external standard using Agilent Chemstation software (Agilent Technologies, Santa Clara, CA, USA). Average lignin molar masses (M_n, M_w) were measured by size exclusion chromatography (SEC): PSS MCX 1000 column and 0.1 M NaOH eluent (T=25°C) with UV detection (280 nm). The molar mass distributions and average molar masses were calculated in relation to polystyrene sulphonate standards with Waters Empower 2 software (Waters, Milford, MA, USA). Several standard analyses were conducted from the 0 min and 240 min samples at KCL Kymen Laboratorio Oy, Finland: chemical oxygen demand, COD(Cr), ISO/DIS 15705; total inorganic carbon, TIC giving the amount of carbon dioxide, SFS-EN 1484:1997; total organic carbon, TOC, SFS-EN 1484:1997.

Capillary electrophoresis (CE) analyses were conducted from the liquid samples to detect small molecular acids formed as lignin degradation products. Structural analyses were performed on the acidified (pH 2.5) and freeze-dried samples as described by Rovio et al. (2011).

Determination of the oxygen consumption

Oxygen consumed in the experiments was calculated from the reactor pressure data by applying the ideal gas law equation and the values of water vapor pressure; the dissolved oxygen was taken into account. It was assumed that lignin oxidation did not occur during the short (0.5–1.5 min) sampling periods. Pressure data from the experiment conducted without lignin were used for estimating the rate constant for the gas-liquid mass transfer model.

Results and discussion

In all experiments, during the first 60 min the lignin reactivity was high, and a very intense stage was observed during the first 20 min. This is readily visible from high oxygen consumption (Figure 1a), from pH decrease (Figure 1b), and fast increase in total charge (Figure 1c). The intense beginning was also clearly seen as degradation of aromatic lignin (Figure 1d) and decreasing content of free phenols (Figure 1e) with a simultaneously increasing proportion of conjugated phenols (Figure 1f). The fast increasing methanol concentration (Figure 1g) correlated with the degradation of aromatic lignin and decreasing content of free phenols. The greatest change in lignin color occurred during the first 30 min, however only in the case of hardwood kraft lignin (Figure 1h). Monitoring the average molar mass of lignin macromolecule (Figure 1i) clearly demonstrates that depolymerization is intense at the beginning of the reaction. According to all observed data, the reactions decelerated after the first 60 min period. After 120 min, the reactions did not significantly advance. Elevating the reaction temperature from 90°C to 110°C increased the oxidation rate of the process, which is in accordance with the general kinetic theory. The effect of pressure was not as significant as that of temperature.

Composition of the starting lignins

The metal analysis results of the starting lignins are presented in Table 2. Elemental compositions and methoxy contents are presented in Table 3. For KL_{SW}, the methoxy content was a bit higher than that reported previously, e.g., by Thring and Griffin (1994), but for KL_{HW}, the methoxy content (26.1%) was surprisingly high when compared both to a recently obtained value of 17.8% (Kubo and Kadla 2006) and also to the S/G ratio (1.28) obtained from the pyrolysis results of the starting KL_{HW} (Rovio et al. 2011). The reason for this is not known. The summative formulae for 100 basic units of KL_{SW} and KL_{HW} (given in Table 3) were computed on the basis of elemental composition and methoxy content. The respective average molecular weights of lignin phenyl propane units were 181 g mol⁻¹ and 216 g mol⁻¹, respectively. Metals in the initial KL_{SW} and KL_{HW} were assumed not to react with oxygen and their share (in total 0.85% and 2.37%; computed from the data given in Table 2) was taken into account in estimating the oxygen consumption by molar lignin to correct the results to the actual lignin content.

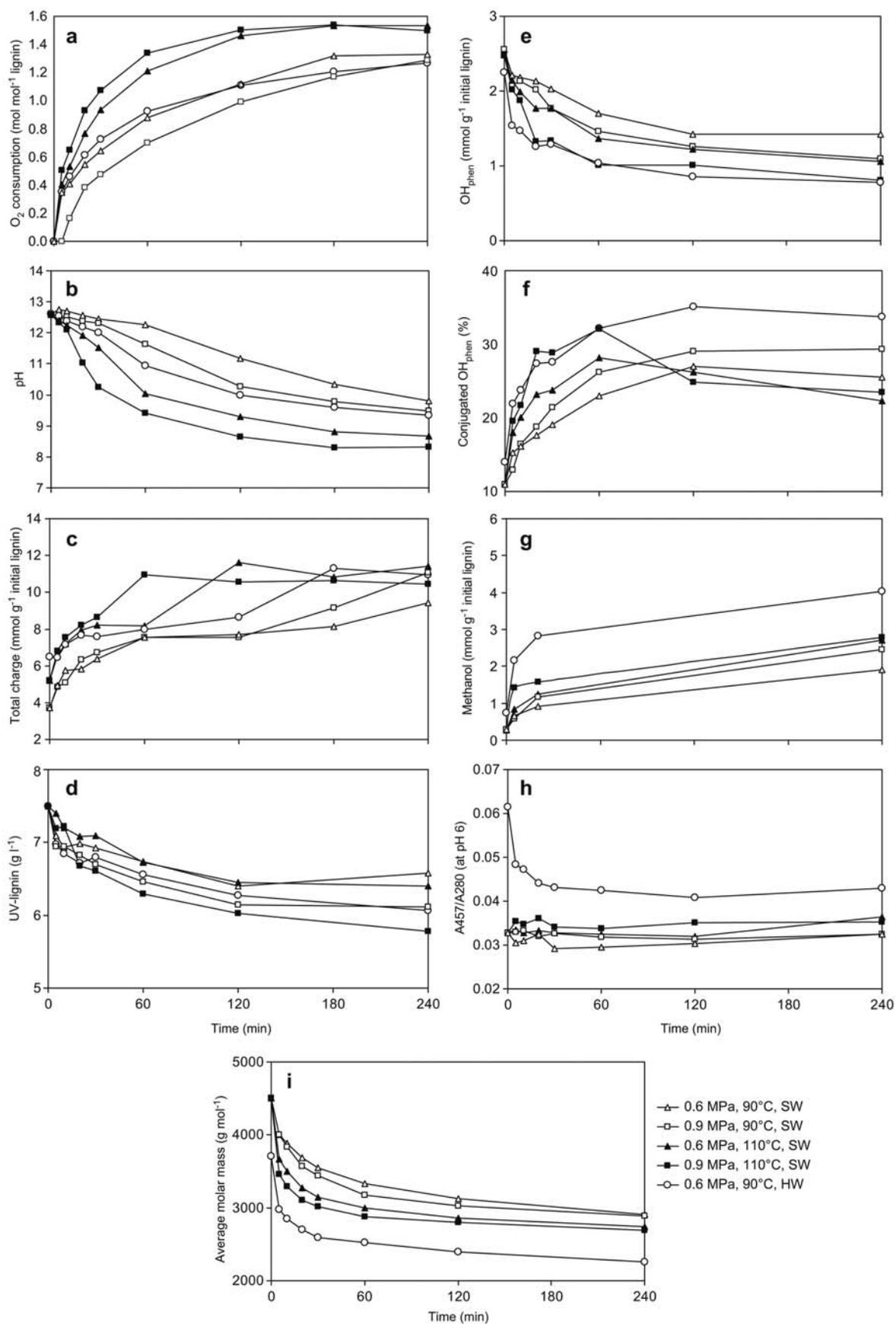


Figure 1 (a–i) Changes of the data indicated on the y-axis as a function of reaction time of oxygen delignification.

Table 2 Metal contents of the initial kraft lignins from softwood (SW) and hardwood (HW).

Element	SW kraft lignin		HW kraft lignin	
	mg kg ⁻¹	SD	mg kg ⁻¹	SD
Sodium (Na)	7194	±225	20 940	±324
Potassium (K)	894	±106	1336	±17
Barium (Ba)		<2	19	±0.1
Calcium (Ca)	102	±2	659	±20
Copper (Cu)		<2		<2
Iron (Fe)	40	±2	100	±1
Magnesium (Mg)	151	±4	416	±7
Manganese (Mn)	43	±1	130	±2
Vanadium (V)	53	±1	87	±1
Zinc (Zn)	7.6	±0.6	12	±1

Oxygen consumption and pH

About half of the oxygen was consumed during the first 20 min in oxidizing KL_{SW} at 110°C under 0.6 MPa and KL_{HW} at 90°C under 0.6 MPa. In oxidizing KL_{SW} at the harshest conditions (110°C, 0.9 MPa) the relation was almost 60% (Figure 1a). The maximum in oxygen consumption, 1.5 mol mol⁻¹ KL_{SW}, was reached in 3 h at 110°C. In the experiments conducted at 90°C, the consumption reached in 4 h was slightly less (1.3 mol for mol⁻¹ KL_{SW} and for mol⁻¹ KL_{HW}). In computing the consumed O₂ based on the reactor pressure decrement, it was assumed that the progress of the O₂ consuming reactions halted during the short sampling periods. This can explain why the obtained values are slightly smaller than the values obtained by Imai et al. (2008), who measured oxygen consumption of KL_{SW} under oxygen-alkali conditions (95°C, 0.8 MPa) and observed an O₂ consumption of 1.8 moles by 200 g lignin (ca. 1 mol lignin) over 4 h.

Here, the mass stoichiometry of oxygen consumption at the end of the reaction corresponded to 0.23–0.27 g O₂ by 1 g KL_{SW}. In industrial O stage, the oxygen consumption has been estimated to be 1 g O₂ by 1 g residual lignin in the course of modeling the industrial oxygen delignification (van Heiningen et al. 2003; Sixta et al. 2006). Also, the O₂ consumption of organic carry over (0.79 g O₂ by 1 g DOC, dissolved organic carbon) is considered in the model. The inorganic reactions that consume oxygen are likely to be

Table 3 Elemental composition and methoxy content of the initial kraft lignins from softwood (KL_{SW}) and hardwood (KL_{HW}).

Sample	C (%)	H (%)	S (%)	O (%)	OCH ₃ (%)
KL _{SW}	62.66	5.84	1.33	30.17	14.37
KL _{HW}	57.48	5.59	2.09	34.84	26.14
Summative formulae					
KL _{SW}	C ₈₅₀ H ₇₈₄ S ₇ O ₂₇₀ (OCH ₃) ₈₃				
KL _{HW}	C ₈₅₀ H ₆₅₂ S ₁₄ O ₂₈₈ (OCH ₃) ₁₈₂				

The summative formulae are calculated for 100 basic units of lignin. The C₈₅₀ basis (instead of C₉₀₀) takes the partial loss of side-chain carbons during the kraft cooking into account (Marton 1971).

included in these estimates as their contribution could not be considered separately. Untreated white liquor, an alkali source in the oxygen stage, is known to reduce the degree of delignification when compared to the usage of oxidized white liquor or sodium hydroxide. This is reported to be due to the presence of the sulfide (Sixta et al. 2006). Analogously, the residual sulfide that enters the O stage within kraft brownstock reduces the degree of delignification because its oxidation potential is partly wasted for oxidation of sulfide ion (HS⁻) to sulfate (SO₄²⁻) instead of residual lignin. Therefore, the difference in O₂ consumption between KL oxidation and industrial pulp oxygen delignification can be partly due to the O₂ consumption of sulfide carry over caused by insufficient brownstock washing and/or incomplete oxidation of white liquor in industrial applications. For instance, in a survey concerning process and design information of industrial oxygen delignification and the following data analysis (Bennington and Pineault 1999), the black liquor carry over to the O stage remained unquantified because of the lack of data reported by the mills surveyed.

In all experiments, the pH was about 12.6 at the onset of the reaction (0 min). At the end of the 4-h reaction, the pH was 2.8–4.3 units lower than at the beginning (Figure 1b). As the temperature was raised, the oxygen consumption was higher and the final pH lower, indicating higher degradation of lignin macromolecule accompanied by higher generation of aliphatic acids. The dominating aliphatic acids in reaction solutions detected by Rovio et al. (2011) were formic, oxalic, acetic, and glycolic acids. Elevating reaction temperature increased the acid formation, especially during the first 60 min, which covered more than half of the total amount of acids formed (Rovio et al. 2011, Figure 1). The pH decrease ceased after the aliphatic acid formation decelerated. Also, in that stage of the reaction, presumably some of the low molecular weight acids have already oxidized to CO₂ and water. At 90°C, especially during the first half of the reaction period, the pH in KL_{HW} solution was clearly lower than in KL_{SW} solution. Correspondingly, during that period more oxygen was consumed in the reactions (Figure 1a) and more aliphatic acids were formed (Rovio et al. 2011, Figure 1) with KL_{HW} than with KL_{SW}. In previous studies, the magnitude of pH decrease in oxidizing residual KL_{SW} (Asgari and Argyropoulos 1998) or alkaline lignin in waste water treatment (Kindsigo and Kallas 2006; Kindsigo et al. 2009) has been reported to be linearly proportional to the reaction temperature.

Total charge

The total charge developed in a logical manner: raising temperature or raising pressure increased the total charge (Figure 1c). The fast increase in total charge was mainly due to high formation of both lignin macromolecule bound acids and small aliphatic acids (Rovio et al. 2011). The charge formation during the 4-h reaction in the SW case was 5.2–7.3 mmol g⁻¹ initial lignin and in the HW case 4.5 mmol g⁻¹. According to the UV method, during the same period the OH_{phen} content decreased 1.1–1.7 mmol g⁻¹ and 1.5 mmol g⁻¹, respectively (results discussed hereinafter).

The interpretation is that four carboxylic acid groups were formed from one phenolic KL_{SW} basic unit and three from one KL_{HW} unit. The observation strongly indicates that the muconic acid type structures reacted further.

TOC, COD, and TIC

Lignin degradation was also followed by TOC (total organic carbon), COD (chemical oxygen demand) and TIC (total inorganic carbon) analysis, which are typical for characterizing pulp mill effluents. The analysis results obtained at 0 and 240 min reaction time are shown in Table 4.

Raising temperature reduced TOC. Raising pressure at 90°C reduced TOC, but did not have an impact at 110°C. In the SW case no great differences were detected in COD reduction, although the COD value obtained under the mildest conditions was highest, i.e., material was least oxidized. For KL_{HW} solution, both the TOC and the COD reductions were greater than for KL_{SW} solution under similar conditions.

Carbon dioxide is formed in the further oxidation reactions of lignin degradation products. According to TIC analyses, in the SW case, 7.0%–8.2% of the carbon from the initial lignin ended up in CO₂. For KL_{HW} this ratio was 8.4%. Increasing both temperature and pressure reduced CO₂ formation slightly. This is probably due to the greater reactivity of phenolic lignin under harsher conditions less favoring the oxidation of aliphatic acids and formation of CO₂. Zhang et al. (2007) measured carbonate formation in oxygen delignification of pine kraft pulp (initial kappa 32.5, 0.8 MPa, 60 min residence time) and reported a value of 13.2 mM, which is ca. half of the formation detected here at the end of the 4-h reaction.

Degradation of aromatic lignin and formation of methanol

One good indicator of the degradation of aromatic structures is the formation of methanol because most lignin precursors

carry methoxy groups, which are released as methanol in the course of the formation of muconic acid type structures and in the further oxidation of quinones. Therefore, in addition to the detection of aromatic lignin content (Figure 1d) and its functionality (Figure 1e and 1f) by UV-method, the concentration of liquid phase methanol (Figure 1g) was followed.

According to the UV method, 12%–23% of the aromatic structures were degraded during the 4-h reaction period, with the lowest degradation observed for KL_{SW} under the mildest conditions. At the onset of the reaction, the OH_{phen} content was 2.5–2.6 mmol g⁻¹ initial lignin (KL_{SW}) and 2.3 mmol g⁻¹ initial lignin (KL_{HW}). During the reaction, the OH_{phen} content decreased 44%–67%. The decline is in line with the results obtained by Asgari and Argyropoulos (1998), who oxidized residual KL_{SW}, but detected the OH_{phen} content by ³¹P NMR. Raising both temperature and pressure reduced the OH_{phen} content. Also, in pulp oxygen delignification, the reduction is related to the severity of the oxygen stage, but even under very harsh conditions, the residual lignin after the stage still contains a considerable amount of phenolic groups (Roost et al. 2003).

Simultaneously with the lowering content of OH_{phen}, the proportion of conjugated OH_{phen} was increased. These conjugated structures were mainly α -carbonyl structures detected by Pyrolysis-GC/MS (Rovio et al. forthcoming). At 110°C, after the first 60 min the proportion of conjugated OH_{phen} clearly decreased and at the end of the reaction the level was lower than in the oxidations conducted at 90°C. This might be due to further reactions of vanillin-like structures at the higher temperature (Gierer and Imsgard 1977). Simultaneous removal of phenolic guaiacyl units and formation of new phenolic α -carbonyl units have been reported in the previous studies (Pasco and Suckling 1998; Yada and Meshitsuka 2007).

For KL_{SW}, 3.1%–4.8% of the carbon from the initial lignin ended up in methanol during the 4-h reaction period. The ratio was 6.9% for KL_{HW}. The molar based reduction of

Table 4 Results of TOC, COD(Cr), and TIC analyses (mg l⁻¹); change (%) between 0 and 240 min.

Parameter of oxygenation	Measured data	TOC, COD, and TIC (mg l ⁻¹)		Δ_{0-240} Change (%)
		At 0 min	At 240 min	
0.9 MPa, 90°C, SW	TOC	4600	3800	-17
	COD	13 000	11 000	-15
	TIC	97	450	364
0.9 MPa, 110°C, SW	TOC	4700	3700	-21
	COD	13 000	11 000	-15
	TIC	100	430	330
0.6 MPa, 90°C, SW	TOC	4600	4100	-11
	COD	13 000	12 000	-8
	TIC	97	480	395
0.6 MPa, 110°C, SW	TOC	4700	3700	-21
	COD	13 000	11 000	-15
	TIC	100	460	360
0.6 MPa, 90°C, HW	TOC	4000	3500	-13
	COD	12 000	9500	-21
	TIC	140	500	257

OH_{phen} was much more modest than the molar based formation of methanol. This might be because the KL was extensively modified so that OH_{phen} could not be properly detected by the UV method, which is not recommended for highly modified lignins (Zakis 1994b). The values given by the UV method are too low for OH_{phen} for modified lignins and for model compounds with more than one aromatic hydroxyl group (Tiainen et al. 1999). However, parallel results obtained by ^{31}P NMR (Rovio et al. 2011) were more plausible, giving ca. 1.5 fold higher concentrations for the initial OH_{phen} , and also giving better agreement with the methanol release. In oxidizing KL_{SW} (Yada and Meshitsuka 2007) under milder conditions than here and in oxygen delignifying residual KL_{SW} (Akim et al. 2001), a slightly smaller formation of methanol or a decrease in methoxy content have been observed. The methanol concentration (1.5 kg t^{-1} pulp) detected during oxygen delignification of SW pulp (kappa no. 37.5) (Pfister and Sjöström 1979) corresponds to formation of 0.83 mmol g^{-1} lignin which is ca. half of the formation measured here.

Lignin color and average molar mass

The main goals of the kraft pulp bleaching sequence are to remove residual lignin and improve pulp brightness. Lignin color observed at pH 6 (Figure 1h) revealed that strong degradation of chromophoric structures in KL_{HW} occurred during the intense beginning of the oxidation. The corresponding development was not observed for KL_{SW} , however, nor was darkening.

The average molar masses of the starting lignins were 4500 g mol^{-1} (KL_{SW}) and 3700 g mol^{-1} (KL_{HW}) (Figure 1i). Reduction in the molar mass of KL_{SW} macromolecule represented a 35% decline in the oxidations conducted at 90°C and a 40% decline in the oxidations conducted at 110°C . For KL_{HW} , the decline was 40%. The results clearly demonstrate that oxidation also degrades ether bonds in lignin.

Conclusions

The results correspond well to general theories regarding the lignin oxidation mechanism, and are also in agreement with the knowledge that hardwood kraft lignin is more reactive than softwood kraft lignin. Increasing the reaction time to over 120 min did not further enhance the lignin degradation. Increasing the reaction temperature, rather than the pressure, had primary significance in increasing the rate of lignin degradation. The results indicate that there is a rather big difference in O_2 consumption between kraft lignin oxidation and residual lignin oxidation in industrial delignification. This was interpreted to be partly due to the O_2 consumption of sulfide carry over in industrial applications, which wastes the oxidation potential.

The samples obtained from this study will be further characterized with advanced analysis methods to distinguish carboxylic acids bound to lignin macromolecule and those bound to the small degradation products of lignin (Rovio et al. forthcoming). The data both from the direct measurements

and advanced analyses will be used to validate a predictive model for lignin oxidation chemistry on the molecular level (Kuitunen et al. 2011).

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