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DESCRIPTION OF OXYGEN-ALKALI DELIGNIFICATION OF KRAFT PULP USING ANALYSIS OF DISSOLVED MATERIAL

BY

MARIA SALMELA

Academic Dissertation
for the Degree of
Doctor of Philosophy

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ABSTRACT

The possibilities of estimating the performance chemistry of an industrial oxygen delignification process were studied by analyzing in detail dissolved pulp material and by using component material balances. One purpose was to estimate the yield and selectivity of this process by characterizing the various reaction products with respect to their origin in pulp. A further aim was to estimate the amount of oxygen that is actually consumed or needed in different reactions during the process and the effect of oxygen charge on selectivity. The research was focused on industrial oxygen delignification process in order to find a way to describe the delignification process which would take account the variables absent in laboratory experiments. The kraft pulps used were Scandinavian softwood (mixture of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*)) and hardwood (silver birch (*Betula pendula*)). The methods were also utilized in laboratory-scale oxygen delignification of bamboo (*Bambusa procera*) kraft pulps.

The use of component material balances to estimate the pulp yield and selectivity of an industrial oxygen delignification process as well as of the laboratory-scale bamboo pulp process proved feasible. The material balances corresponded to a pulp yield of 97-98 % for the industrial wood pulps and yields of 95-98 % for the laboratory bamboo pulps. It was estimated that roughly 70-80 % of the softwood and ~60 % of the hardwood pulp material dissolved derived from lignin. The selectivity of bamboo pulps was comparable to that of the birch pulps.

Estimations for the origin of oxygen on the basis of the dissolved reaction products revealed that 39-80 % of the charged oxygen was consumed during the oxygen delignification stage. The results suggested a molecular oxygen consumption of 0.6-1.0 kg/BDt per unit of kappa number reduction for softwood and 1.0-2.0 kg/BDt per Δkappa unit for hardwood kraft pulps. Oxidation of components (Na_2S, $Na_2S_2O_3$, and Na_2SO_3) in the oxidized white liquor (OWL) consumed a considerable portion of the molecular oxygen, especially in cases where the sulfide concentration in OWL was high.

It was observed that birch kraft pulps were more susceptible to degradation, which was seen in greater amounts of dissolved hydroxy monocarboxylic acids and volatile acids compared to that of softwood pulps. In spite of the somewhat different chemical composition of bamboo pulps, compared to wood kraft pulps, the oxygen delignification of bamboo kraft pulp resulted, for example, in the formation of the same carbohydrate-derived degradation products (*e.g.*, aliphatic carboxylic acids) as obtained during the oxygen delignification of birch kraft pulp.

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PREFACE

This work was carried out at the Laboratory of Applied Chemistry, Department of Chemistry, University of Jyväskylä during years 2002-2006.

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Despite their everlasting amazement for my choice of field, my parents, Marketta and Martti, have given me their whole-hearted support during my years of study for which I'm deeply grateful. My loving thanks to Jaakko for his patience and understanding due to my numerous nights and weekends spent at the laboratory and writing this thesis.

Jyväskylä, March 2007

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LIST OF ORIGINAL PAPERS

I Ala-Kaila, K., Salmela, M. & Alén, R. 2002. Estimation of pulp yield in industrial oxygen-alkali delignification of softwood kraft pulp. Nordic Pulp Paper Res. J. 17(4), 401-404.

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II Ala-Kaila, K., Salmela, M. & Alén, R. 2002. Estimation of selectivity in industrial oxygen-alkali delignification of softwood kraft pulp. Nordic Pulp Paper Res. J. 17(4), 405-409.

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III Salmela, M., Alén, R. & Ala-Kaila, K. 2004. Fate of oxygen in industrial oxygen-alkali delignification of softwood kraft pulp. Nordic Pulp Paper Res. J. 19(1), 97-104.

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CONTENTS

ABBREVIATIONS

AAS	Atomic absorption spectrometry
ADt	Air dry (10 % moisture) metric ton of pulp
AOX	Absorbable organic halides
BDt	Bone dry (moisture-free) metric ton of pulp
BL	Black liquor
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
DP	Dissolved reaction products
DS	Dissolved solids
EA	Effective alkali ($NaOH + ½ Na_2S$)
FID	Flame ionization detector
GC	Gas chromatography
HexA	Hexenuronic acid
HP	Hewlett Packard
HUT	Helsinki University of Technology
IC	Ion chromatography
ICP-AES	Inductively-coupled plasma atomic emission spectrometry
i.d.	Inside diameter
ISTD	Internal standard
LCC	Lignin-carbohydrate complex
Mod.kappa	Modified kappa number (corrected for HexAs)
MSD	Mass selective detector
o.d.	Oven dry
OWL	Oxidized white liquor
RSD	Relative standard deviation
SCAN	Scandinavian Pulp, Paper & Board Testing Committee
SFS	Finnish Standards Association
TAPPI	The Leading Technical Association for the Worldwide Pulp, Paper, and Converting Industry
TIC	Total inorganic carbon
TMS	Trimethylsilyl
TOC	Total organic carbon
UV	Ultraviolet
Vis	Visible

1 INTRODUCTION

Kraft pulping, which uses NaOH and Na_2S in delignification of wood and non-wood, is the most widely used process in the production of chemical pulps (McDonough, 1996; Alén, 2000a). As a part of the kraft pulping process, oxygen-alkali delignification (generally referred to as oxygen delignification) has acquired an important role in lowering the residual lignin content in pulp prior to actual bleaching since the 1970s, when it was commercialized. Without compromising the physical properties using oxygen and alkali to remove about half of the lignin in unbleached pulp is an environmentally friendly way of decreasing the formation of harmful bleaching effluents and an economically favorable way of reducing the use of expensive bleaching chemicals (McDonough, 1996; Alén, 2000a). Although some two- or multi-stage oxygen delignification processes can reach a delignification degree of ~70 % (Carter *et al.*, 1997; Steffes *et al.* 1998), oxygen delignification cannot usually remove more than 35-50 % of the residual lignin (typically <5 % of material**)** before detrimental oxidative carbohydrate degradation takes place. The loss in selectivity has been cited as a major drawback to the continued implementation of this environmentally benign technology. Hence an important objective in current oxygen delignification research is to achieve a more fundamental understanding of the chemical factors governing delignification and carbohydrate damage to pulp (Lucia *et al.*, 2002).

The chemical basis for delignification with oxygen is the electrophilic character of oxygen and its ability to attack electron-rich sites in lignin (Gierer and Imsgard, 1977a; Gratzl, 1987; McDonough, 1996). Molecular oxygen alone is a relatively weak oxidizing agent; however, during its stepwise reduction to water more active, but, less selective oxygen species are formed (such as $OO^{-}\bullet$, HOO^{-}, and $HO\bullet$). Thus, process selectivity is greatly affected by the radical chemistry of active oxygen species since they react with both lignin and carbohydrates. As a consequence, oxygen delignification is less selective than the subsequent bleaching. Moreover in addition to the removal of lignin, carbohydrates (mainly hemicelluloses), and extractives are also affected by oxygen and alkali, leading to a wide range of water-soluble reaction products (Malinen, 1974; Pfister and Sjöström, 1979; Alén and Sjöström, 1991). Apart from degraded lignin material these reaction products consist mainly of hydroxy carboxylic acids, formic and acetic acids, carbohydrates (hemicellulose residues), methanol, and carbon dioxide.

Lignin and carbohydrate reactions together create a loss in yield, *i.e.*, percentage loss of pulp material. Pulp yield can easily be measured gravimetrically in laboratory experiments. Such experiments are usually performed with laboratory-cooked pulp, which is properly washed, cooled, and stored before oxygen delignification. Pulp samples of this kind can probably never be maintained in a transient state comparable to that obtained for pulp samples from a mill-scale continuous process. This transient state, *i.e.*, leaching performance and chemical concentrations inside the fibers, can significantly affect the performance of the process and the delignification response in different types of pulps and processes (Ala-Kaila and Reilama, 2001). There is also a risk of losing fine pulp particles in screening when measuring the gravimetric yield. Thus, it would be beneficial if pulp yield could be estimated directly on the industrial scale.

Although many researchers have reported methods (Süss and Kronis, 1998; Genco *et al.*, 2000; Luonsi and Halttunen, 2000; Rööst and Jönsson, 2001; Tamminen, 2005) of evaluating delignification responses using dissolved material analysis, such as COD and TOC analyses, the present study involved further analysis of the various individual components in the process liquor. Other examples of this kind of compound-based method of evaluation include attempts to use, for instance, the content of hydroxy carboxylic acids and/or lignin monomers to monitor kraft pulping and oxygen delignification (Alén *et al.*, 1991; Alén, 1993).

A tool for the accurate determination of selectivity would also be of great value in comparing different process concepts and further developing the oxygen delignification process. Selectivity can be defined by the extent of carbohydrate degradation per unit lignin removed or as the ratio of desired reaction products to the total amount of all reaction products (Reeve, 1996). In the case of oxygen delignification, the amount of soluble lignin-derived products formed as a fraction of the total pulp material dissolved during the process should thus correlate with the selectivity of this treatment. However, with respect to delignification, and especially to bleaching, selectivity is commonly regarded as the ratio between the reduction in pulp viscosity and in the kappa number, *i.e.*, Δviscosity/Δkappa (Olm and Teder, 1979; Sjöström, 1981; McDonough, 1996). Selectivity can also be more appropriately expressed chemically as the relative rate of reaction of a particular bleaching chemical with lignin compared with that of other pulp components, that is, as the ratio between the rates of delignification and carbohydrate degradation (Ek *et al.*, 1989; Reeve, 1996; Iribarne and Schroeder, 1997).

Oxygen is a relatively cheap chemical and for several years it has been added excessively just to ensure the presence of sufficient amounts. For this reason, there is not necessarily a linear correlation between oxygen charge and degree of delignification if one studies mill process parameters (Bennington and Pineault, 1999). Excessive oxygen addition can even be detrimental to delignification. When investigating the degree and selectivity of oxygen delignification more attention has been paid to process variables other than the oxygen charge, including alkali charge, temperature, pressure, and reaction time (Olm and Teder, 1979; Li *et al.*, 1996; McDonough, 1996).

Since in industrial oxygen delignification systems oxygen is used as a quantitative charge of 0.7-3.0 % on pulp (Reeve, 1989; Bennington and Pineault, 1999) with an intensive gas mixing pulse while in laboratory reactors oxygen is applied at constant pressure and often excessively, it has been difficult on the basis of laboratory delignification experiments to determine the real consumption or the exact amount of reacted oxygen. However, recently Imai *et al.* (2005) developed a device for measuring the actual amount of oxygen consumed with lignin reactions in a laboratory reactor. Also, by assuming that change in pressure during laboratory delignification is only due to oxygen, the decrease in pressure can be linked to oxygen consumption (Thompson and Corbett, 1976; Berry *et al.*, 2002). Nonetheless, there remains a difference in the way molecular oxygen is charged in a laboratory and on the industrial scale.

All the above mentioned differences between laboratory and industrial oxygen delignification lead to the need to find a way to describe the process which would take account the variables absent in laboratory experiments. Also a better understanding of the various reactions occurring in oxygen delignification and the chemical composition of dissolved organic material would benefit the development of more accurate methods of estimating the selectivity and yield of this process. One purpose of this study was to estimate the yield and selectivity of an industrial oxygen delignification process by characterizing the various reaction products with respect to their origin in pulp. Another aim was to estimate the amount of oxygen that is actually consumed or needed in different reactions during the process. In other words, the interest was to clarify where the charged and consumed oxygen "goes", *i.e.*, the fate of oxygen. One additional purpose was to determine the effect of oxygen charge on selectivity. The kraft pulps used were made from Scandinavian softwood (mixture of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*)) and hardwood (silver birch (*Betula pendula*)).

The same methods were also utilized in the laboratory-scale oxygen delignification of bamboo (*Bambusa procera*) kraft pulp, as its composition is not markedly different from that of wood kraft pulps. Although industrial process was the main object of this research, laboratory-scale was implemented in this case since it was not possible to obtain industrial bamboo pulp samples. So far an oxygen stage is not commonly applied to unbleached kraft bamboo pulps; therefore the knowledge of the chemical composition of the oxygen delignification effluent of bamboo kraft pulp would offer additional information of use in the further development of this application, especially with respect to its selectivity. Bamboo is an attractive raw material for chemical pulp as, due to its long fibers, it has strength properties comparable to those of softwood pulp (Rydholm, 1965; Misra, 1980). Its close structural (lignin and hemicellulose contents) resemblance to woods is also the main reason why kraft pulping of bamboo provides an acceptable degree of delignification as well as high yield and viscosity. Non-wood resources are important raw materials in countries where wood is not available in sufficient quantities to meet the demand for pulping and papermaking. Non-wood fibers are also expected to play an increasingly important role in the pulp and paper industry owing to diminishing forest resources, environmental issues, growing paper consumption, and advancing technologies in non-wood utilization (Atchison, 1998; Hammett *et al.*, 2001).

2 OXYGEN DELIGNIFICATION

2.1 General aspects

Oxygen delignification, also sometimes referred to as oxygen bleaching, is today a well-established technique and is used in plants around the world (McDonough, 1996; Alén, 2000a). Environmental concerns and awareness have been the main reasons for the widespread implementation of oxygen delignification in the production of kraft pulp, although, the process has some operational cost advantages as well. Oxygen-stage effluents can be recycled to the kraft recovery system by way of the brown stock washers and the use of this stage decreases the need for a delignifying oxidizing chemical (*e.g.*, chlorine dioxide or ozone) in the subsequent bleaching process. This leads to a major reduction in the environmental load of bleach plant effluents, decreasing AOX, BOD, COD, and color levels. In addition, oxygen is less expensive than the other bleaching chemicals and oxidized white liquor (OWL) usually provides the necessary alkali for the oxygen stage at low cost. Thus, oxygen is a beneficial delignification agent: it is relatively cheap, stable, non-toxic, and readily available.

The main disadvantage of the process is its high capital cost, but increased demand on the mill recovery system can also be a drawback (McDonough, 1996; Alén, 2000a). The increased load on the recovery boiler is 2-4 % measured as total dry substance (Idner and Kjellberg, 1989; Gullichsen, 2000) and if OWL is used, the increased load on the causticizing department is 5 %. Problems with non-selectivity can be avoided if a suitable carbohydrate protector is used and if the degree of delignification is not too high (usually no more than ~50 %).

In a typical application of the oxygen delignification process, unbleached pulp is discharged from the last brown stock washer, charged with NaOH and/or OWL, preheated in a pressure steam mixer and fed to the high-shear, medium-consistency mixer, where oxygen gas is added (McDonough, 1996; Gullichsen, 2000). The pulp then passes to an up-flow pressurized oxygen reactor. After the oxygen-stage, the pulp is washed to remove caustic, lignin, and other dissolved material. The washing filtrate of the oxygen stage is returned to the last brown stock washer by means of a counter-current flow.

Industrial oxygen delignification can be either a single-stage or a multi-stage system (McDonough, 1996; Alén, 2000a; Gullichsen, 2000; Pikka *et al.*, 2000). Generally delignification is done in the temperature range 85-115 °C and at a pressure of 0.3-1.0 MPa at either medium (10-14 %) or at high (25-30 %) pulp consistency. Overall treatment time in the reactor is between 30 to 60 minutes. As a carbohydrate protector magnesium salts (usually $MgSO_4$) are used in low amounts (0.05-0.1 % Mg^{2+} of o.d. pulp).

To achieve cost effective bleaching with a low environmental impact, it is important that the pulp enters the bleach plant at a low kappa number. The discharge kappa numbers in oxygen delignification are generally 8-20 (average 13.7) and 8-12 (average 10.2) for softwoods and hardwoods, respectively (Carter *et al.*, 1997). The level of delignification varies from 28 % to 67 % for softwoods and from 29 % to 55 % for hardwoods when measured as the decrease between the digester and post oxygen kappa number (means 47 % and 40 %).

2.2 Chemistry of oxygen

In its ground state molecular oxygen is a stable diradical which has a tendency to react with appropriate substrates at regions of high electron density (Sjöström, 1993; McDonough, 1996). As a substrate such as lignin is oxidized, oxygen is reduced to water in a four-step process by one-electron transfer (or in two steps by two-electron transfer) involving intermediate products as hydroperoxy radicals (HOO•), hydrogen peroxide (HOOH) and hydroxyl radical (HO•) as well as their corresponding organic intermediates (Fig. 1). In alkaline conditions the hydroperoxy radical is ionized (OO^-•) and hydrogen peroxide and the hydroxyl radical are also partly present in their dissociated form (HOO^- and O^-•, respectively). As a molecule, oxygen is a relatively weak, although selective, radical agent, but the radical species resulting from oxygen reactions are more reactive and some significantly less selective, such as the hydroxyl radicals. The reactions that take place in oxygen delignification are similar to those in hydrogen peroxide bleaching since both are performed in alkaline conditions and include the same intermediate reaction products: oxygen converting partly to H_2O_2 and *vice versa* (Gierer and Imsgard, 1977a; Sjöström, 1993).

The radical chain reactions occurring during oxygen delignification are extremely complex involving a number of organic species derived from both lignin and carbohydrates (Gierer and Imsgard, 1977a; Gratzl, 1987; Alén, 2000a). Strong alkaline conditions and high temperature are required to induce the reactions and to attain reasonable reaction rates. The reactivity of active oxygen species produced during oxygen delignification, and thus selectivity, is significantly dependent on the reaction conditions such as the reaction temperature and pH of the medium (Renard *et al.*, 1975; Ek *et al.*, 1989; Yokoyama *et al.*, 1999; Guay *et al.*, 2002). According to investigations of the reaction rate of hydroxyl radicals with lignin and carbohydrate models, the rate constant for a given pair of lignin and carbohydrate models lies between 5 and 6 (Ek *et al.*, 1989). Thus, hydroxyl radicals attack lignin 5-6 times faster than carbohydrate structures, although different reaction rates have also been observed. According to Yokoyama *et al.* (2005), the reaction selectivity of hydroxyl and oxyl anion radicals (at pH 11.8 and 13.1, respectively) between lignin and carbohydrate model compounds was 2.1 and 0.3, respectively.

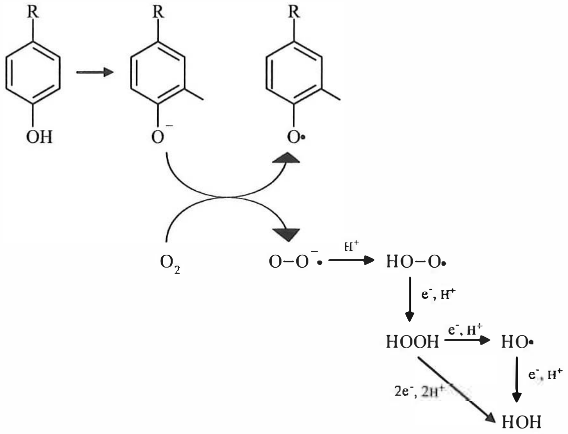


FIGURE 1 Initial oxidation reactions in oxygen delignification (redrawn with modifications from Fu *et al.* (2004)).

The selectivity of the process is greatly affected by the presence of trace quantities of transition metals (Fe, Co, Cu, and Mn) which catalyze the decomposition of peroxides to hydroxyl radicals. These reactive and indiscriminate radicals are thought to be mainly responsible for the degradation of polysaccharides. Experiments have indicated that molecular oxygen is not in fact capable of degrading carbohydrates without the presence of a radical initiator such as lignin or metals (Akim, 1973; Guay *et al.*, 2000, 2002). Magnesium ions (generally in the form $MgSO_4$) are used as carbohydrate protector, which precipitate as magnesium hydroxide in the presence of alkali and deactivate metal ions through an association of some kind, possibly by absorbing the metal ions or by forming complexes with them (Sjöström, 1981; Minor, 1996).

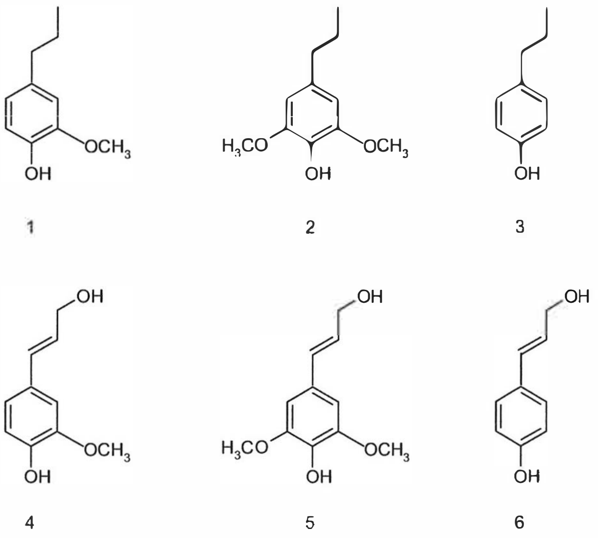
Oxygen delignification occurs in a very heterogeneous medium and the behavior of the pulp components is affected by several factors: treatment conditions, diverse raw materials, various reactive structures, fiber structure, and the location of the fiber components (lignin/carbohydrates) as well as their physical and chemical properties (Pekkala, 1983). Mass-transfer limitations are also a serious consideration in oxygen delignification, since oxygen, which has very low water solubility, must be applied to pulp as gas (Reeve, 1996;

Gullichsen, 2000). Therefore, gas-to-liquid and liquid-to-solid transfer of oxygen to the reaction site on the pulp fiber are necessary to initiate the oxidation of lignin (Iribarne and Schroeder, 1997).

2.3 Delignification reactions

2.3.1 Lignin

Lignin is a three-dimensional amorphous polymer consisting of randomly linked phenylpropane units (Gellerstedt, 1996; Alén, 2000b). Softwood lignins ("guaiacyl lignins") are mainly composed of *trans*-coniferyl alcohol units (Fig. 2, structure 4) whereas hardwood lignins ("guaiacyl-syringyl lignins") are composed of *trans*-coniferyl and *trans*-sinapyl alcohol units (structure 5). Bamboo, as well as other grass lignins, can generally be classified as "guaiacyl-syringyl lignins" (Tai *et al.*, 1990; Bhargava, 1993; Chen *et al.*, 1993; Alén, 2000b). A typical feature of bamboo lignin is that, like aspen lignins (Alén, 2000b), it contains 5-10 % esters of the *p*-hydroxyphenyl structural units (Fig. 2, structure 3) and have a higher proportion of phenolic hydroxyl groups than wood lignins. The structural units in the lignin polymer are joined together by ether linkages (Fig. 3, linkages between units A and B and D and E) or by carbon-carbon bonds (B-C in Fig. 3).



1 2 3

4 5 6

FIGURE 2 Main building blocks of lignin: guaiacylpropane (1), syringylpropane (2), and *p*-hydroxyphenylpropane (3) and primary precursors of the lignin biosynthesis; *trans*-coniferyl alcohol (4), *trans*-sinapyl alcohol (5), and *trans*-*p*-coumaryl alcohol (6) (Brunow, 2006).

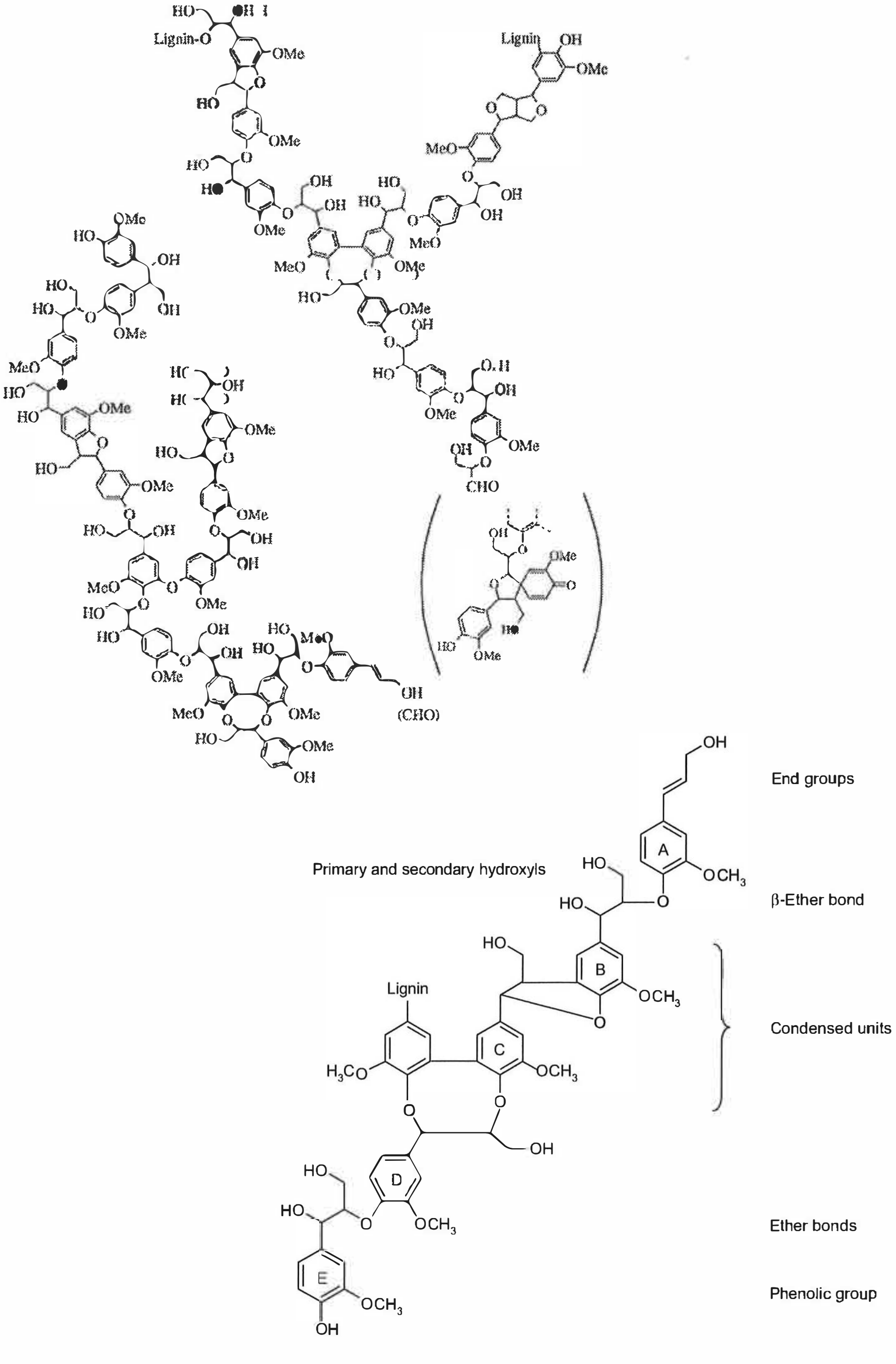


FIGURE 3 A structural scheme for softwood lignin (top) and some specific features of lignin (bottom) (Brunow *et al.*, 1998; Syrjänen, 2000; Brunow, 2006).

Various functional groups in aromatic ring and in the side chain affect the properties and reactivity of lignin (Sjöström and Westermark, 1999). The content of these phenolic and aliphatic hydroxyl groups as well as methoxyl and carbonyl groups varies among wood species. The most important functionality in lignin from a reactivity point of view is the presence of free phenolic hydroxyl groups; such groups are rather scarce since most of the hydroxyls form linkages with other phenylpropane units (Gellerstedt, 1996). The content of phenolic hydroxyl groups after pulping is approximately 30 per 100 phenylpropane units (C_6C_3). In most chemical reactions involving lignin, the phenolic phenylpropane units are attacked preferentially.

Free phenolic and enolic hydroxyl groups in lignin play a key role in the initial reactions of oxygen delignification, when alkali converts these groups into more reactive phenolate and enolate anions thereby providing electron-rich sites vulnerable to attack by oxygen (Gierer and Imsgard, 1977a; Gierer, 1986; Dence, 1996; McDonough, 1996; Alén, 2000a). The first phase in the oxygen reactions after this lignin activation is the formation of phenoxy radicals with electron transfer from the ionized phenolic groups to oxygen (Fig. 1). In the process superoxide ion radicals ($OO^{-\circ}$) are formed. The different mesomeric forms of the resulting resonance-stabilized phenoxy radicals react with O_2 or $OO^{-}\bullet$ forming hydroperoxides (Fig. 4, Scheme A, radical phase not shown). Incidentally, hydroxyl radicals can originate from these hydroperoxide units by the homolytic splitting of the O-O bond through reactions catalyzed by transition metals. The hydroperoxide intermediate, existing in part as the corresponding anion in an alkaline environment, can subsequently undergo an intramolecular nucleophilic reaction at an adjacent site, forming a dioxoetane structure. Rearrangements of this structure lead to the formation of oxirane structures and muconic acid derivatives (Fig. 4, Scheme A), thereby introducing hydrophilic groups to lignin and enhancing solubility. The rupture of the C_α-C_β bond joining two lignin monomers, which leads to lignin fragmentation, results from the rearrangement of a dioxoetane structure, or epoxide structure as in Fig. 4 (Scheme B), formed in the lignin side chain. These and further reactions with oxygen or superoxide ion radicals produce some lignin monomers as well as aliphatic low-molecular-mass degradation products such as carboxylic acids and methanol.

The phenoxy radicals are, in principle, also capable of coupling reactions and thus forming new carbon-carbon bonds between lignin units (McDonough, 1996; Argyropoulos and Liu, 2000). These condensation reactions are obviously undesirable because they increase the molecular size of lignin (decrease solubility) and are more resistant to further reactions. Owing to the restricted mobility of the phenoxy radicals in lignin, however, it is unlikely that these reactions occur extensively during oxygen delignification.

In addition to the desired reactions with lignin, which increase solubilization, competing reactions, which lead to the formation of unwanted by-products and do not contribute to higher brightness or lower lignin content, also occur during oxygen delignification (Reeve, 1996). These reactions include, for example, reactions with already dissolved lignin.

It is now generally accepted that lignin is chemically linked to carbohydrates (mainly to hemicelluloses) in native wood and in pulp (Alén, 2000b; Lawoko *et al.*, 2003; Backa *et al.*, 2004). These covalently linked aggregates known as lignin-carbohydrate complexes (LCC) can also be formed during pulping. Lawoko *et al.* (2003) have proposed that 90 % of the residual lignin in kraft pulp is covalently linked to carbohydrates; mostly bound to xylan and glucomannan. Part of the lignin apparently also forms a network structure with xylan and glucomannan. The activity of the lignin can be dependent on the polysaccharide it is bound to (Lawoko *et al.*, 2004) and the LCC bond might be a major restriction in gaining a more efficient oxygen delignification (Backa *et al.*, 2004).

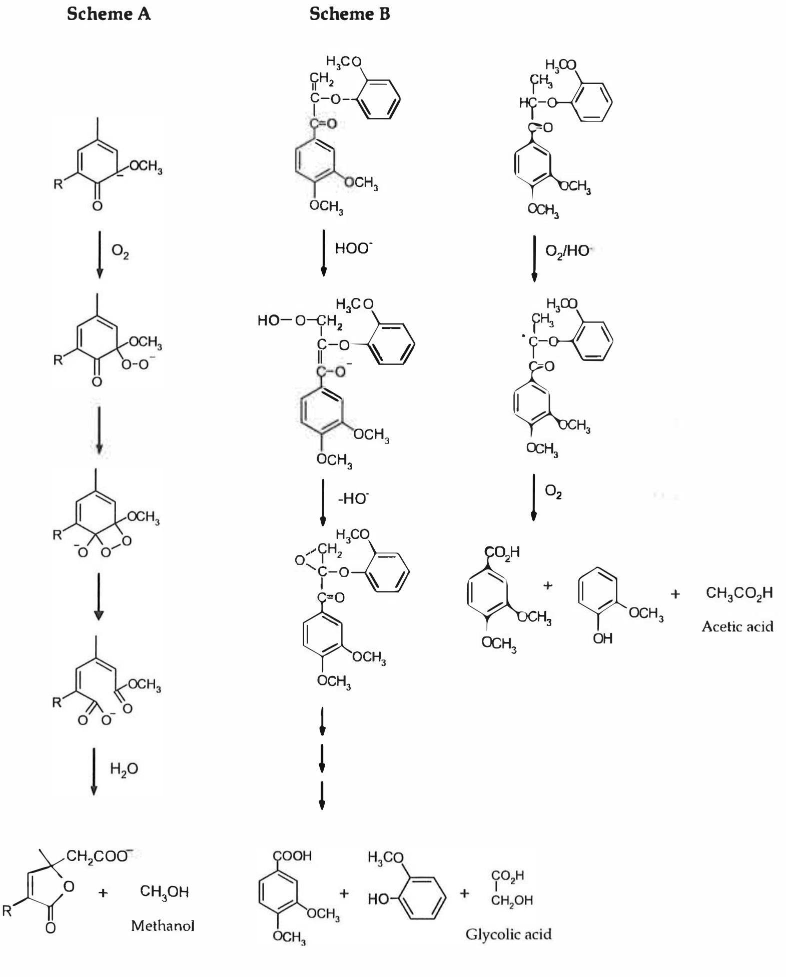


FIGURE 4 Examples of proposed reaction paths for the formation of some of the reaction products of lignin during oxygen delignification (Gierer and Imsgard, 1977a; Soultanov *et al.* 2000).

2.3.2 Carbohydrates

Pulp (or wood) carbohydrates are polysaccharides consisting of cellulose and various hemicelluloses (Alén, 2000b). Cellulose is composed of a chain of β-D-glucopyranose units joined together with glycosidic bonds. Hemicelluloses are heteropolysaccharides and are composed mainly of D-glucose, D-mannose, D-galactose, D-xylose, and L-arabinose units together with uronic acid units.

Cellulose and hemicelluloses are the main components contributing to pulp strength (cellulose 65-75 % and hemicelluloses 20-30 % of unbleached pulp (Alén, 2000a)), and it is desirable that these components do not react with oxygen or in general with any bleaching chemical (Reeve, 1996). Alkaline treatment mainly removes hemicelluloses, although some simultaneous loss of cellulose is unavoidable because of the similarity in structure and reactivity.

The reactions involving pulp polysaccharides during oxygen-alkali treatment can be classified into the following main categories (Malinen, 1974, 1975; McDonough, 1996): stabilization of the reducing end-group, peeling reaction starting from the reducing end-group, peeling reaction starting from the stabilized end-group and cleavage of the polysaccharide chain. The reactions responsible for carbohydrate degradation are random chain cleavage, which may occur at any point of along the chainlike molecule, and endwise peeling, by which units on the end of the chain are attacked and removed. Transition metals promote random chain cleavage by catalyzing the formation of reactive oxygen radicals that attack the carbohydrate chain leading to chain rupture.

The reaction that mainly causes yield losses in cooking, "peeling", is not as dominant in oxygen delignification as is the random chain cleavage (Sjöström, 1993; Gellerstedt, 1996). The peeling reaction starts with reducing end groups (carbonyl groups), which have already been converted to stable polysaccharide end groups (metasaccharinic acid-type) during cooking; in fact, at the end of kraft pulping virtually all carbohydrate end groups have been converted to carboxylic acids. Also, oxygen itself converts any remaining or new reducing end groups generated by random chain rupture to stable oxidized form (aldonic acid groups).

Carbohydrate chain cleavage is initiated by the action of the hydroxyl radicals that are produced during lignin degradation (Sjöström, 1993; McDonough, 1996). They oxidize the primary and secondary alcohol groups in polysaccharides with reactions involving the removal of hydrogen atoms from hydroxyl-substituted carbons and the formation of hydroxyalkyl radicals, which are converted to carbonyl structures by oxygen (Figs. 5-6, A). The ketol structures so formed readily undergo β-alkoxy elimination (Figs. 5-6, B), leading to cleavage of the glycosidic bond between the carbohydrate units and generating new reducing end-groups at the fragmented polysaccharide chain (susceptible to oxidation and step-wise polymerization, *i.e.,* peeling) (Dence, 1996).

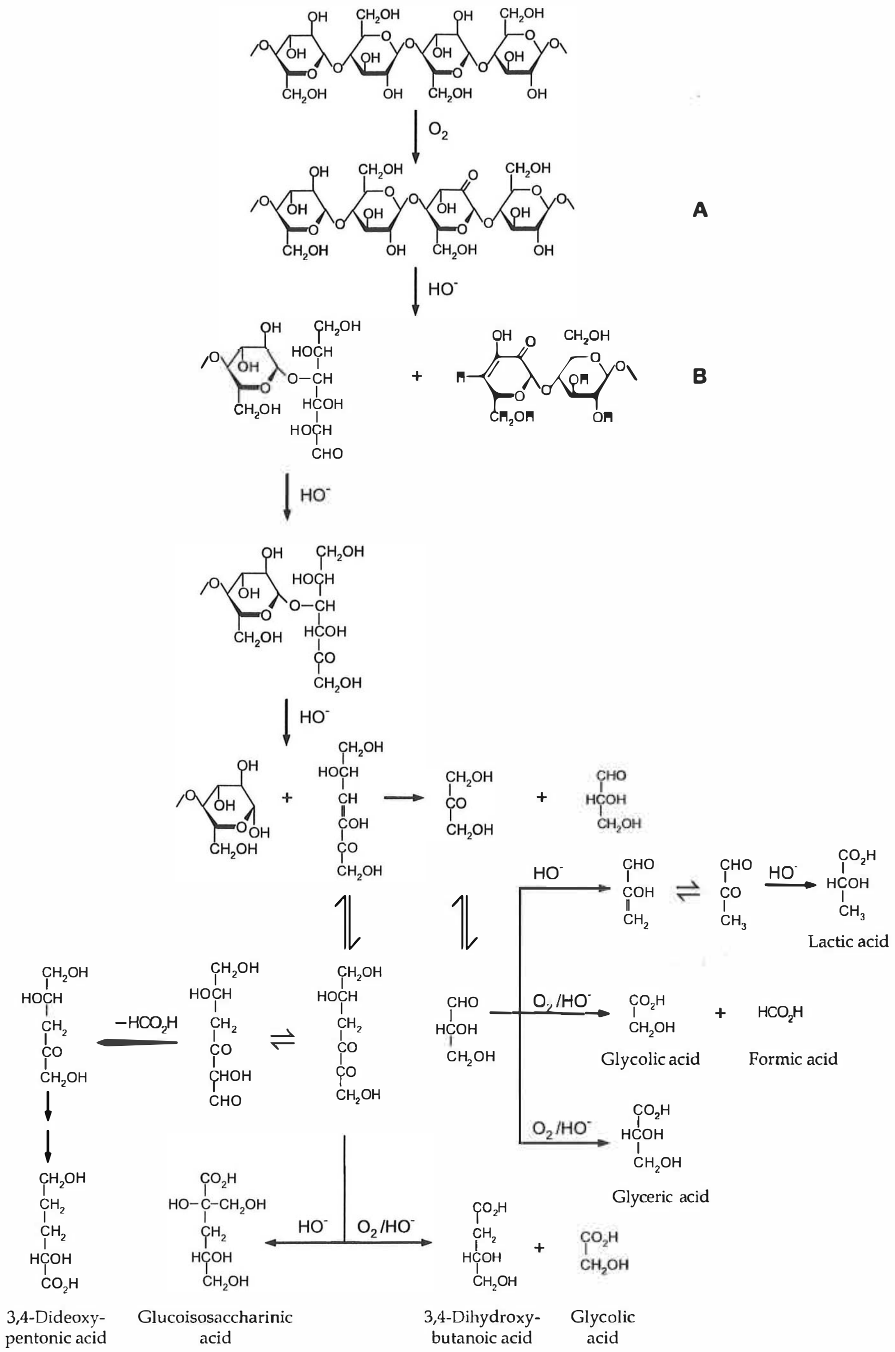


FIGURE 5 Examples of proposed reaction paths for the formation of the main reaction products of hexosans (cellulose and glucomannan) during oxygen delignification (Ericsson *et al.*, 1973; Löwendahl and Samuelson, 1974; Malinen, 1974, 1975; Sjöström, 1993). The alternative stereoisomers of hydroxy acids (the different configuration mainly at C-2) are not shown.

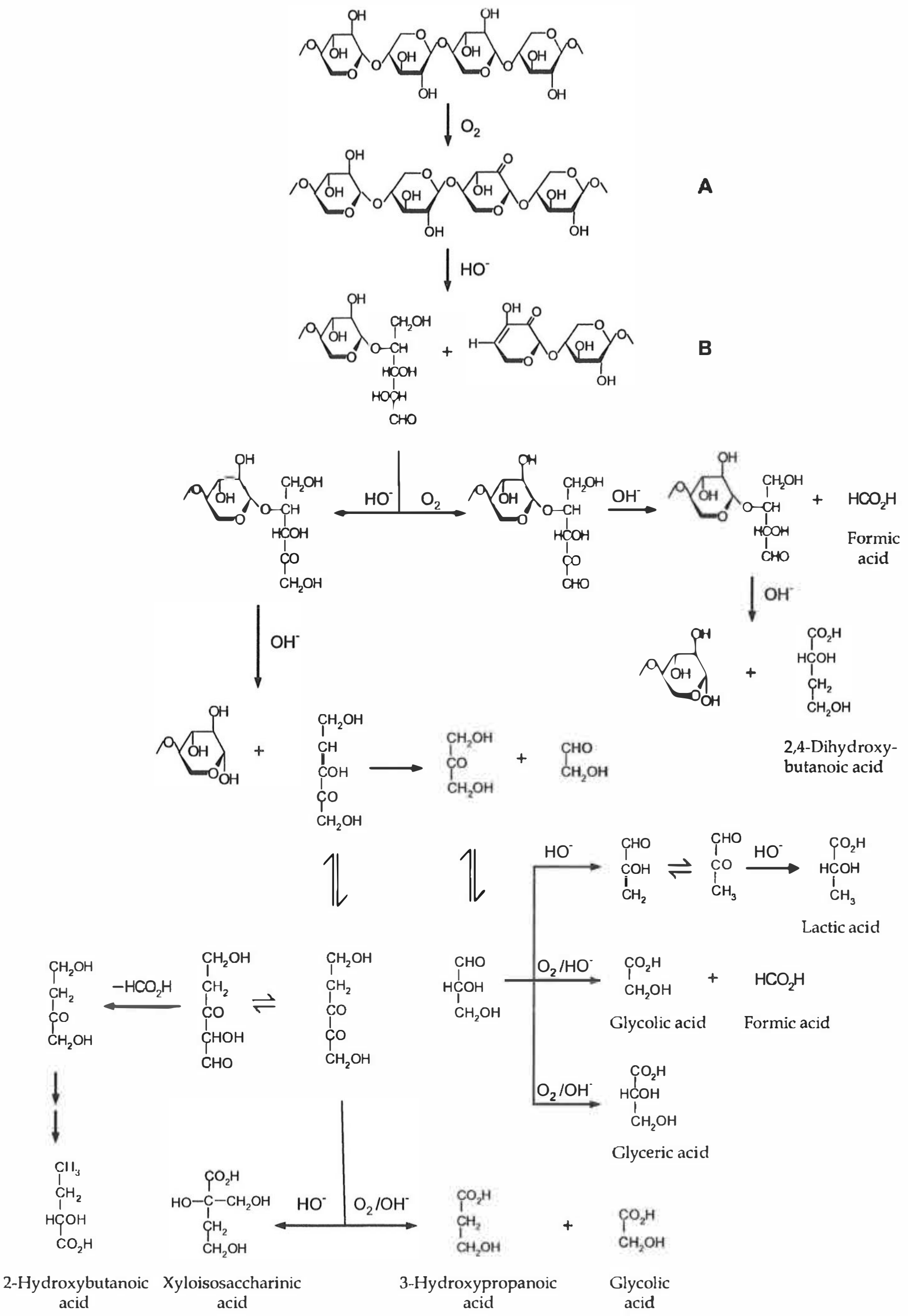


FIGURE 6 Examples of proposed reaction paths for the formation of the main reaction products of pentosans (xylan) during oxygen delignification (Kolmodin and Samuelson, 1971, 1973; Malinen 1974, 1975; Sjöström, 1993). The alternative stereoisomers of hydroxy acids (the different configuration mainly at C-2) are not shown.

The reactions following oxidation of the alcohol groups can also result in oxidation of the ketol structure and formation of a 2,3-diketo unit, which can be further oxidized to dicarbonyl acid (Alén, 2000a). The diketo unit can also be converted to a carboxyl-containing furanosidic structure. These reaction paths do not lead to depolymerization.

The hexenuronic (4-deoxy-4-hexenuronic) acid (HexAs) groups in pulp xylan are converted from 4-*O*-methylglucuronic acid groups of wood xylan during kraft pulping by β–elimination of methanol (Sjöström, 1993; Buchert *et al.*, 1995; Jiang *et al.*, 2000). HexAs react with several bleaching chemicals, such as chlorine dioxide and ozone, but they are believed to be unreactive in the alkaline oxygen treatment (Buchert *et al.*, 1995; Vuorinen *et al.*, 1996; Allison *et al.*, 1999; Jiang *et al.*, 2000). However, the content of HexAs in the pulp can be reduced during delignification owing to peeling of xylan fragments. There is also a possibility that HexAs might be formed during oxygen delignification which is indicated by a study of Antonsson *et al.* (2003). It is now known that hexenuronic acids among few other components, such as extractives and some structures with double bonds and/or carbonyl groups, contribute to the kappa number measurement (Li and Gellerstedt, 2002; Li *et al.*, 2002; Shin *et al.*, 2004, 2006), which is commonly used as measure of pulp lignin content. Thereby kappa number used as an indicator of delignification degree can be misleading if the effect of HexAs is not taken into account, especially in the case of hardwood pulps, which have a greater content of HexAs than softwoods.

2.3.3 Extractives

The heterogeneous group of compounds known as wood extractives include *e.g.*, terpenoids, steroids, fats, waxes, and various phenolic constituents (stilbenes, lignans, tannins, and flavonoids) (Sjöström and Westermark, 1999). The amount of extractives that remain in the pulp after kraft pulping is quite low, especially for softwood: 0.1-0.3 % (Gellerstedt, 1996; Shin *et al.*, 2004, 2006). For hardwood the amount is 0.5-1.0 % depending on the species. After oxygen delignification the extractives content has been found to be 0.05-0.11 % and 0.32-0.43 % for pine and birch pulps, respectively (Shin *et al.*, 2004, 2006). Thus, oxygen delignification removes approximately half of the residual extractives in pulp, which are mainly chromophore-containing extractives (Shin and Kim, 2006).

Because of their low concentration in unbleached pulp, extractives play a relatively minor role in determining the outcome of oxygen delignification, although they presumably react with oxygen to some extent (Dence, 1996; Holmbom, 2000).

2.3.4 Reaction products

As a consequence of the above mentioned reactions, pulp constituents degrade and form a wide range of reaction products. For example, in kraft pulping over 350 simple degradation compounds have been identified, of which about 150 are aromatic compounds originating from lignin (Gratzl, 1991) while the number of identified carboxylic acids in alkaline pulping liquors exceeds 100 (Niemelä and Alén, 1999). The carboxylic acids formed during oxygen delignification are, for the most part, the same as those found in the kraft pulping liquors although their absolute amounts and relative proportions differ (Malinen and Sjöström, 1975b; Sjöström, 1977; Niemelä *et al.*, 1985; Alén, 2000a). The main compounds dissolved during oxygen delignification are, in addition to degraded lignin fragments, aliphatic carboxylic acids (hydroxy monocarboxylic and dicarboxylic acids, formic and acetic acids, carbohydrates (hemicellulose fragments), methanol, and carbon dioxide (Malinen 1975; Pfister and Sjöström 1979; Alén and Sjöström 1991). Proposed mechanisms for the formation of some of the main reaction products during oxygen delignification are illustrated in Figures 4-6 and in Appendix 1.

Oxidation of lignin results mainly in aliphatic mono- and dicarboxylic acids (in addition to CO_2). It has been suggested that these are formed for the most part as a result of the breakdown of an aromatic ring. (Soultanov *et al.*, 2000, 2003). Most of the hydroxy dicarboxylic acids dissolved during oxygen delignification are probably formed from lignin (Merriman *et al.*, 1966; Malinen, 1975; Renard *et al.*, 1975; Young and Gierer, 1976; Pfister and Sjöström, 1979) although small amounts of dicarboxylic acids are formed from cellulose and xylan as well (Löwendahl and Samuelson, 1974; Samuelson and Sjöberg, 1974). Some lignin oxidation studies have shown the total yield of non-aromatic acids (dicarboxylic, hydroxy, and fatty acids) formed from birch and pine dioxan lignin to be 25 % and 15.6 %, respectively, of the reacted compound (Soultanov *et al.*, 2003). Other investigations have revealed that approximately 80 % of the total acids formed during oxygen-alkali treatments of lignin were oxalic, formic and acetic acids (Grangaard, 1963). In addition, succinic and glycolic acids have been found to be among the main acidic reaction products of isolated lignins (Soultanov *et al.*, 2000). Monoacids as well as oxalic, succinic, and malonic acids may arise from both aromatic and side chain structures (Young and Gierer, 1976; Soultanov *et al.*, 2003). Other aliphatic lignin degradation products that have been identified are fumaric, malic, lactic, and glyceric acids (Grangaard, 1963; Young and Gierer, 1976). Also small amounts of acetone and acetaldehyde can be products of lignin degradation, perhaps from the side chains (Scholander *et al.*, 1974; Young and Gierer, 1976; Soultanov *et al.*, 2000).

Lignin-derived monomers represent only a minor fraction (total amount 0.2-0.4 % of pulp) of the lignin removed in oxygen delignification (Alén and Sjöström, 1991). Among these monomers are, e.g., 4-hydroxybenzaldehyde, benzoic acid, 1,4-benzenedicarboxylic acid, acetovanillone, vanillin, vanillic acid, ferulic acid, 5-formylvanillin, 5-carboxyvanillin, and acetoguaiacone (Scholander *et al.*, 1974; Renard *et al.*, 1975; Alén and Sjöström, 1991).

Carbon dioxide has been found to be the most abundant constituent in the liquor (Scholander *et al.*, 1974; Pfister and Sjöström 1979; Soultanov *et al.*, 2000). CO_2 is apparently produced in the oxidation of lignin side chains as well as aromatic rings (Soultanov *et al.*, 2000), and certain carboxylic acids (acetic acid, α-aryl, α-keto, β-keto, β,γ-unsaturated carboxylic acids, and muconic acids) are known to decarboxylate to form carbon dioxide (Fessenden and Fessenden, 1994; Huang *et al.*, 1997). It can also be formed during carbohydrate degradation (Löwendahl and Samuelson, 1974; Guay *et al.*, 2000). On the basis of earlier research (Soultanov *et al.*, 2000; Murphy *et al.*, 2003) it can be concluded that in oxygen delignification the principal source of carbon dioxide is lignin. This was supported by studies where CO_2 production correlated with the amount of residual lignin in pulp whereas cellulose did not have an affect on the amount of CO_2 produced (Murphy *et al.*, 2003). Further proof of carbonate formation is that it seems to correlate both with the reduction in kappa number and with the dissolved lignin to a certain point of delignification (Chai *et al.*, 2003a). However, the experiments by Fu *et al.* (2004) suggested that if delignification proceeds below kappa number 7 (delignification degree >65 %), the majority of the carbon dioxide originates from oxidation of carbohydrates. Some estimations of the relative origin of carbon dioxide have also been made (Samuelson and Sjöberg, 1974): about 67 % coming from lignin, 11 % from cellulose and 22 % from hemicelluloses.

Most of the hydroxy monocarboxylic acids originate from carbohydrates (Kolmodin and Samuelson, 1972, 1973; Malinen, 1975) as a result of peeling reactions. The peeling and stabilization reactions of cellulose and glucomannans proceed in a similar manner resulting in similar reaction products (Malinen, 1974). The main peeling products of cellulose and glucomannans have been found to be formic, lactic, glycolic, 3,4-dihydroxybutanoic, 3-deoxypentonic, and glucoisosaccharinic acids (Malinen, 1974; Kolmodin and Samuelson, 1972; Samuelson and Sjöberg, 1974). Characteristic products of xylan degradation are glycolic, 3-hydroxypropionic, 2,4-dihydroxybutanoic, and xyloisosaccharinic acids (Kolmodin and Samuelson, 1973; Samuelson and Sjöberg, 1974; Malinen and Sjöström 1975a). Small three-carbon acids (lactic, glycolic, and glyceric acids) are also formed from side chains of lignin (Young and Gierer, 1976; Gierer and Imsgard, 1977a). Table 1 summarizes some of the main hydroxy acids and their proposed sources according to the literature.

TABLE 1 Main hydroxy acids formed in oxygen-alkali delignification of kraft pulp and pulp components. Numbers refer to the sources shown in the footnote

Acid	Pine kraft pulp	Birch kraft pulp	Cellulose and glucomannan	Xylan	Lignin
Monocarboxylic acids:					
Formic	1, 2, 3	1, 4	1,5,6	1	9
Acetic	1, 2, 3	1, 4	1,5,6		9
Glycolic (hydroxyacetic)	1, 2, 3	1,4,7	1, 5,6	1,8	9,10
Lactic (2-hydroxypropanoic)	1, 2, 3	1, 4,7	1, 5,6	1,8	9,10
3-Hydroxypropanoic (2-deoxy-glyceric)	1, 2, 3	1, 4,7	6	1,8	
Glyceric (2,3-dihydroxypropanoic)	1, 2, 3	1,4,7	1, 5,6	1,8	
2-Hydroxybutanoic		4		8	
4-Hydroxybutanoic	3	4			
2,4-Dihydroxybutanoic (3-deoxy-tetronic)	1, 2, 3	1,4,7	6 (traces)	1, 8	
3,4-Dihydroxybutanoic (2-deoxy-tetronic)	1, 2, 3	1,4,7	1,5,6	1,8 (traces)	
3-Deoxy-*erythro/threo*-pentonic	1, 2, 3	1,4,7	1,5,6	1,8	
Xyloisosaccharinic (3-deoxy-2-(hydroxymethyl)tetronic)	1, 2, 3	1,4,7		1,8	
Anhydroglucoisosaccharinic	3	4			
3-Deoxy-*arabino*-hexonic (β-glucometasachharinic)	2	7	5,6	8	
3-Deoxy-*ribo*-hexonic (α-glucometasachharinic)	2				
Glucoisosaccharinic, α- and β-forms (3-deoxy-2-(hydroxymethyl)-*erythro/threo*-pentonic)	1, 2, 3	1, 4	1,5,6	8	
2-Deoxy-*erythro*-pentonic	2		6		
Galactometasaccharinic	3	4			
Dicarboxylic acids:					
Oxalic (ethanedioic)	2, 3		6		9,10
Maleic (*cis*-butenedioic)					9,10
Fumaric (*trans*-butenedioic)					9,10
Tartronic (hydroxypropanedioic)	2,3	4	6		
C-Methyltartronic (hydroxymethylpropanedioic)	3		6		
Succinic (butanedioic)	2, 3	4			9,10
Malic (hydroxybutanedioic)	3	4			10
3-Deoxy-*threo*-pentaric	3	4	6		
Glucoisosaccharinaric (3-deoxy-2-C-(hydroxymethyl)-pentaric)	3	4			
Malonic (propanedioic)	2				9,10

1 (Malinen, 1974, 1975; Malinen and Sjöström, 1975a), 2 (Pfister and Sjöström, 1979), 3 (Alén and Sjöström, 1991), 4 (Ristolainen and Alén, 1998), 5 (Kolmodin and Samuelson, 1972), 6 (Löwendahl and Samuelson, 1974), 7 (Samuelson and Sjöberg, 1974) (oxygen-alkali treatment of birch wood), 8 (Kolmodin and Samuelson, 1973), 9 (Renard *et al.*, 1975), 10 (Soultanov *et al.*, 2003)

Formic and acetic acids are formed as a result of both carbohydrate and lignin reactions (Grangaard, 1963; Merriman *et al.*, 1966; Kolmodin and Samuelson, 1972, 1973; Samuelson and Sjöberg, 1974; Renard *et al.*, 1975; Young and Gierer, 1976). Volatile acids can be a result of monosaccharide unit degradation or side-group fragmentation. A probable major source of formic acid is xylan and other polysaccharides (Samuelson and Sjöberg, 1974), and acetic acid can be formed from the remaining acetyl groups (after pulping) in galactoglucomannans and hardwood xylan (Kolmodin and Samuelson, 1973; Sjöström, 1977). Lignin-derived formic and acetic acids do not necessarily originate from the side-chains of lignin, although it seems plausible (Young and Gierer, 1976).

According to the literature (Samuelson and Sjöberg, 1974; Dence, 1996; Zhu *et al.*, 2000) the probable main source of methanol in oxygen delignification is lignin. During kraft pulping the main origin of methanol is 4-*O*-methylglucuronic acid groups of xylan which are partly converted to 4-deoxy-4-hexenuronic acid (HexA) groups (Jiang *et al.*, 2000; Chai *et al.*, 2003b). Most, if not all, of the methoxyl groups linked to hemicelluloses are liberated in cooking. On the contrary, most of methoxyl substituents in lignin have not yet been demethylated during pulping (Zhu *et al.*, 2000), and thus they can be hydrolyzed in the downstream processes, such as oxygen delignification. In addition to methoxyl groups (Fig. 4), methanol can be formed from the oxidative degradation of the phenolic ring (Kratzl *et al.*, 1974; Scholander *et al.*, 1974; Soultanov *et al.*, 2000). Hardwoods produce more methanol than softwoods owing to the variation in methoxyl group content in xylan and lignin (Zhu *et al.*, 2000).

3 EXPERIMENTAL

3.1 Pulp and liquor samples

3.1.1 Softwood

Samples of industrial Scandinavian softwood kraft pulp (mixture of Scots pine (*Pinus sylvestris*) 70 % and Norway spruce (*Picea abies*) 30 %) were taken before and after a two-stage oxygen delignification process. The total pulping process utilized a continuous cooking digester followed by two diffuser washers for brown stock washing, a screen room decker, and two medium consistency oxygen delignification reactors with a double diffuser in post-oxygen washing (Fig. 7). The actual pulp sampling sites were the pulp feed to the oxygen delignification stage and pulp after the second reactor. These sampling sites were chosen so as to exclude the effect of the counter-current filtrate. Due to the location of the feed pulp sampling site and to the process configuration in this mill, the weight of alkali had to be excluded from the material balances by calculation. Otherwise, the material balances (*i.e.,* the difference between the blow and feed samples) would have not fully represented the result of the reactions in the oxygen delignification process. The sampling procedure was designed to correspond to the retention time (55-80 min) between the sampling points.

Four different trials were done, of which the test runs numbered 3 and 4 were carried out on the same day with the intention of maintaining the other process conditions, with the exception of the amount of oxygen, unchanged between runs. Trials 1 and 2 are reported in the original papers I and II (where they are referred to as Run #1 and Run #2, respectively) and trials 3 and 4 are discussed in paper III (Runs #1 and #2, respectively). The main process parameters for the test runs are shown in Table 2.

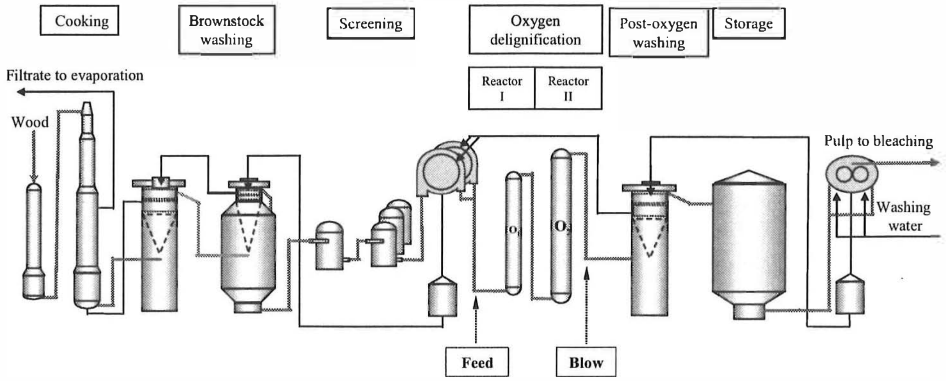


FIGURE 7 Process configuration of the mill producing softwood kraft pulp (I; II; III). Sampling sites marked Feed (=supplying reactor with material) and Blow (=discharging contents of the reactor).

TABLE 2 Process parameters for oxygen delignification of softwood kraft pulp in test runs 1 & 2 (I; II), and 3 & 4 (III)

Parameter		1	2	3	4
		Reactor[1] I / II	Reactor I / II	Reactor I / II	Reactor I / II
Production rate	ADt/d	1300	1300	1350	1350
O_2	kg/ADt	6 / 2	4 / 4	6 / 2	14 / 2
OWL[2]	kg/ADt	9 / 0	5 / 5	13 / 0	12 / 0
NaOH	kg/ADt	14 / 0	0 / 0	5.5 / 0	5.5 / 0
$MgSO_4$	kg/ADt	2.5 / 0	2.5 / 0	2.5 / 0	2.5 / 0
Temperature	°C	85 / 91	87 / 91	90 / 91	91 / 92
Pressure	MPa	0.64 / 0.35	0.67 / 0.33	0.69 / 0.3	0.63 / 0.3

[1] For reactor, see Fig. 7
[2] Oxidized white liquor

Pulp samples from both sampling sites were centrifuged separately for a few minutes (up to 35 % consistency) until additional filtrate was no longer obtained from the centrifuge. This procedure was performed within 15 minutes of the initial sampling. The recovered filtrates were stored as such in a freezer pending further analysis. The centrifuged pulp was washed with deionized water for 30 minutes at a constant temperature (50 °C) and rate of mixing. The pulp was centrifuged again after washing and stored for analysis.

In addition, samples were taken of OWL used in the process during trials 3 and 4.

3.1.2 Hardwood

Samples of Scandinavian silver birch (*Betula pendula*) kraft pulp were taken during three large-scale runs, mainly differing from each other in the amount of oxygen and in the amount and quality of the charged OWL. These trials are reported in paper IV, where they are referred to as Run 1, 2 and 3, respectively.

In each run, two pulp samples were taken before and two samples after the oxygen delignification stage. The final results were reported as an average of these two samples. The process utilized a continuous cooking digester followed by two diffuser washers for brown stock washing, a screen room decker, and one medium-consistency oxygen delignification reactor with a double diffuser for post-oxygen washing (Fig. 8). The actual pulp sampling sites were the feed to the oxygen delignification stage after the addition of alkali and steam, and pulp from the reactor blow tank. In the material balances of these samples, the effect of alkali addition was automatically cancelled out and needed no further calculatory corrections. The main process parameters for the different test runs are shown in Table 3. The sampling procedure was designed to correspond to the retention time (60-70 min) between the sampling points.

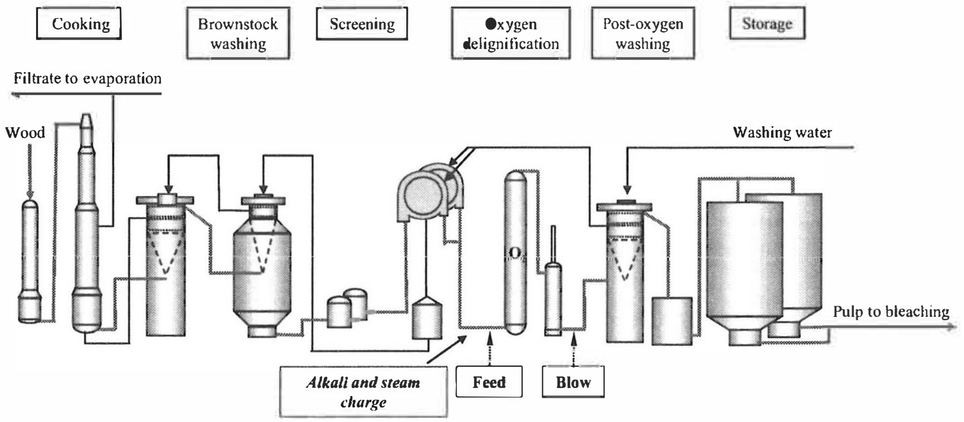


FIGURE 8 Process configuration of the mill producing hardwood kraft pulp (IV). Sampling sites marked Feed and Blow.

TABLE 3 Process parameters for oxygen delignification of hardwood kraft pulp (IV)

Parameter		1	2	3
Production rate	ADt/d	1040	1250	1310
O_2	kg/ADt	5.5	15.9	11.1
OWL	kg/ADt	14.5	27	37
NaOH	kg/ADt	-	-	-
$MgSO_4$	kg/ADt	-	2.5	2.5
Temperature	°C	96	98	98
Pressure	MPa	0.5	0.5	0.5

Pulp samples from both sampling positions were centrifuged separately for a few minutes (up to 35 % consistency) until additional filtrate was no longer obtained from the centrifuge. This procedure was performed within 15 minutes of the initial sampling. The recovered filtrates were stored as such in a freezer pending further analysis. The centrifuged pulp was washed with deionized water, centrifuged again after washing, and stored for analysis.

In addition, samples were taken of the OWL used in the process.

3.1.3 Bamboo

Kraft pulp was prepared on a laboratory-scale from Vietnamese bamboo (*Bambusa procera*) (Table 4). Bamboo chips were screened (SCAN-CM 40:94), air dried, and stored at a dry solids content of ~92 %. Kraft pulping was done in a CRS Autoclave System CAS 420 using an oil bath and stainless steel autoclaves (6 x 1.25 L). Each autoclave was charged with 200 g of o.d. chips. Two cooking experiments each with a different alkali charge were done (Table 5). At the end of each cook, the autoclaves were cooled in cold water. The black liquor was separated from the pulp and the pulp was thoroughly washed, dewatered in a centrifuge and homogenized, and the total yield determined gravimetrically.

TABLE 4 Composition of the bamboo material (Vu *et al.*, 2004)

Component	Content (% of o.d. feedstock)
Carbohydrates	68.6
Lignin	25.8
Extractives	0.8
Proteins	2.6
Ash	2.2
Silica	0.7

TABLE 5 Cooking conditions of the kraft pulping of bamboo (V)

Parameter		Pulp 1	Pulp 2
EA[1], on o.d. bamboo as NaOH	%	14	20
Sulfidity	%	25	
Liquor-to-bamboo ratio	dm^3/kg	4	
Cooking temperature	°C	165	
Time from 80 °C to maximum temperature	min	85	
Time at maximum temperature	min	80	

[1] Effective alkali

One-stage medium consistency oxygen-alkali delignification was carried out in a Quantum high intensity mini mixer using the conditions shown in Table 6. After oxygen delignification, the liquor was filtrated from the pulp and the pulp was thoroughly washed by diluting it to 3 % consistency with deionized water, mixed well, and dewatered. This washing procedure was repeated four times after which the pulp was centrifuged and homogenized.

TABLE 6 Oxygen delignification conditions used for the bamboo kraft pulp (V)

NaOH, on o.d. pulp	%	2
$MgSO_4$, on o.d. pulp	%	0.5
Consistency	%	10
O_2 -pressure	MPa	0.5
Temperature	°C	90
Treatment time	min	60

3.2 Analytical determinations

All the liquor samples were filtrated (0.45 µm) prior to the analyses to separate possible fine fibers from the liquor. For every sample (pulp or liquor) at least two replicate analyses were performed. In addition to the analyses described below, the industrial pulp samples were analyzed for consistency before centrifugation.

3.2.1 Pulp samples

Kappa number and viscosity

The centrifuged pulp samples were analyzed for kappa number and intrinsic viscosity according to standard methods SCAN-C 1:00 and SCAN-CM 15:99, respectively.

Extractives

The content of extractives was determined by extracting the air-dry pulps (~2 g) with acetone (150 mL) for 4 hours in a Soxhlet apparatus (Holmbom, 1999). After extraction, initial evaporation of the solvent was done with a vacuum rotaevaporator and final drying of the residue under a stream of nitrogen gas.

Hexenuronic acids and carboxyl groups

The content of HexAs was determined as furan derivatives by UV spectroscopy at 245 nm after selective acid hydrolysis of the pulp samples according to the "HUT method" described by Tenkanen *et al.* (1999) with the exception of the heating mode; heating under reflux was applied in contrast to the pressure vessel and oil bath used in the original method.

The total amount of carboxyl groups was analyzed by the magnesium ion exchange method according to Sjöström and Haglund (1961).

Inorganics

Metals and sulfur were analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) after wet acid digestion of the milled (a Retsch SM 100 Mill) samples in a microwave oven (Milestone Ethos Touch Control) using concentrated nitric acid and hydrogen peroxide.

Silica was measured by atomic absorption spectroscopy (AAS) after wet acid digestion of the samples using concentrated nitric acid and tetrafluoroboric acid.

Elemental analysis (C, H, and N) of the wood pulps was determined by LECO CHN-600 and of the bamboo pulp by a VarioEL III analyzer.

3.2.2 Liquor samples

Dissolved solids and carbon

The amount of dissolved solids was determined according to standard methods SFS 3008 and TAPPI T 650 om-99.

Total organic (TOC) and total inorganic carbon (TIC) were analyzed using a Shimadzu TOC-5000A analyzer.

Lignin

The lignin content in the effluents was characterized by a Beckman DU 640 UV spectrophotometer at 280 nm (Alén and Hartus, 1988) using the following absorptivity values for kraft and oxygen-alkali-treated lignin.

Softwood liquor: 24.3 $\mathrm{dm}^3/(\mathrm{g}{\star}\mathrm{cm})$ (*kraft*) and
22.6 $\mathrm{dm}^3/(\mathrm{g}{\star}\mathrm{cm})$ (*oxygen-treated*)
(Alén and Hartus, 1988; Väänänen, 2000)
Hardwood liquor: 20.3 $\mathrm{dm}^3/(\mathrm{g}{\star}\mathrm{cm})$ (*kraft*) and
20.0 $\mathrm{dm}^3/(\mathrm{g}{\star}\mathrm{cm})$ (*oxygen-treated*)
(Alén and Hartus, 1988)
Bamboo liquor: 27.8 $\mathrm{dm}^3/(\mathrm{g}{\star}\mathrm{cm})$ (*for both*) (Vu *et al.*, 2003)

Carbohydrates

Carbohydrates were hydrolyzed by sulfuric acid and the resulting monosaccharides were analyzed as their per(trimethylsilyl)ated (TMS) derivates by an HP 5890 II GC/FID instrument (Table 7) (Vuorinen and Alén, 1999). Dialysis (molecular mass cut-of 3500) was performed for black liquors of bamboo before the carbohydrate analysis.

Tappi std.

TABLE 7 GC/FID analysis of carbohydrates

Parameter	GC/FID
Column	DB-1701 60 m ∗ 0.32 mm (i.d.), film thickness 0.25 μm
Temperature program	100 °C for 2 min 100 °C → 185 °C (2 °C/min) 185 °C for 27 min 185 °C → 280 °C (39 °C/min) 280 °C for 15 min
Injector temperature	290 °C
Detector temperature	300 °C
Carrier gas	N_2
ISTDs (internal standards)	Xylitol/glycerol/myo-inositol

The amount of polysaccharides were calculated from the results of the analysis by conversion factors in which the relative composition of (galacto)glucomannan in wood was applied (Alén, 2000b). The ratio galactose:glucose:mannose in softwood is 0.1-0.2:1:3-4 or 1:1:3, depending on the amount of galactose. From this the amounts of the polysaccharides can be calculated according to the following equations:

glucose (in galactoglucomannan) = 0.3 * mannose

galactoglucomannan = galactose + mannose + 0.3 * mannose

glucose (in cellulose) = glucose (total) - 0.3 * mannose.

The quantity of arabinoglucuronoxylan can be obtained by summing the amounts of arabinose and xylan.

Following the same principle, the ratio of glucose to mannose in hardwood glucomannan is 1:1-2 (Sjöström, 1993; Alén, 2000b), which results in a formula where

glucose (in glucomannan) = 0.7 * mannose.

The analytical method causes some error in the results since some carbohydrates are lost during hydrolysis. Therefore the amounts of glucomannans, xylan, and cellulose were multiplied by factors of 1.146, 1.128, and 1.168, respectively. These factors have been determined previously with carbohydrate model compounds (Väänänen, 2000).

Carboxylic acids

The volatile acids, formic and acetic acids, were determined as their benzyl ester derivatives with an Agilent 6850 GC/FID instrument (Alén *et al.*, 1985; Niemelä and Alén, 1999). The molar response factors between the internal standard and the peaks derived from the acids were determined separately using standard sample solutions.
Aliphatic hydroxy carboxylic acids were quantified as their TMS derivatives with an Agilent 6850 GC/FID instrument and identified by an Agilent 6890/5973 GC/MSD instrument (Alén *et al.*, 1984; Niemelä and Alén, 1999).

Identification of the hydroxy acids was based on a software library search (database Wiley 7th Ed.) and data from previous studies. Response factors used for the quantitative calculations were based on the data given by Alén *et al.* (1984). The parameters for the gas chromatographic analyses of the acids are shown in Table 8.

TABLE 8 GC analyses of the aliphatic carboxylic acids

Parameter	Volatile acids	Hydroxy acids	
	GC/FID	GC/FID	GC/MSD
Column	HP-5 30 m * 0.32 mm (i.d.), film 0.25 μm	HP-5 30 m * 0.32 mm (i.d.), film 0.25 μm	Rtx-5 and Supelco Equity™-5 30 m * 0.25 mm (i.d.), film 0.25 μm
Temperature program	60 °C for 3 min 60 °C →150 °C (3 °C/min) 150 °C → 230°C (15 °C/min) 230 °C for 5 min	60 °C for 5 min 60 °C →200 °C (2 °C/min) 200 °C → 290°C (70 °C/min) 290 °C for 15 min	Same temperature program as for GC/FID
Injector temperature	280 °C	290 °C	
Detector (FID) temperature	280 °C	300 °C	
Carrier gas	N_2	N_2	He
ISTD	Crotonic acid	Xylitol	Xylitol

The quantity of oxalic acid analyzed by GC does not correspond to the actual amount in the liquor since it partly decomposes during analysis. Therefore, in some of the softwood samples oxalic acid was measured by IC along with the sulfur ions (see the sub-section: "Inorganics and other properties").

Methanol

The gas chromatographic method (Table 9) was also applied in the determination of methanol in the liquors (Dahlman *et al.*, 1999). A regression line calculated on the basis of calibration standards was used to estimate the MeOH concentrations of the test samples by interpolation.

It should be mentioned that direct column injection is not the most suitable method of analyzing methanol in black liquors owing to their high content of dissolved solids, especially inorganic salts, which foul the column (Chai *et al.*, 1998; Zhu *et al.*, 2000). However, since the liquors used in this study contained substantially lower amounts of solids than pulping black liquors, the method was thought appropriate for this purpose.

TABLE 9 GC/FID analysis of methanol

Parameter	GC/FID
Column	Rt-QPLOT 15 m $*$ 0.32 mm (i.d.), film thickness 10 μm
Temperature program	80 °C for 5 min 80 °C → 200 °C (40 °C/min) 200 °C for 2 min
Injector temperature	220 °C
Detector temperature	220 °C
Carrier gas	N_2

Inorganics and other properties

Sodium content was measured with a Lange M7 DC II flame photometer.

The thiosulphate, sulfite, and sulfate ion contents of the filtrates and of the OWL samples were analyzed by ion chromatography (a Dionex 4500 instrument) using a conductivity detector. This method was also applied to the determination of oxalic acid.

OWL was also analyzed for total alkali (SCAN-N 2:88) and TIC content determined with a Shimadzu TOC-5000A analyzer.

3.3 Estimations

3.3.1 Fate of oxygen

In this study, the amount of oxygen consumed in various reactions during the delignification process was determined by applying a theoretical approach combined with the analytical results. This necessitated investigation of the total amount of oxygen bound to the dissolved reaction products. The data on oxygen content discussed here are also included in Appendix 2 and the calculations needed to estimate the origin of oxygen are explained in Appendix 3.

Oxygen in reaction products

The oxygen content of softwood pulp lignin was obtained from earlier studies (Sun and Argyropoulos, 1995; Jiang and Argyropoulos, 1999) reporting an oxygen content of 27.9 % for kraft lignin and an average of 29.8 % for oxygen-delignified pulp lignin. Values for birch pulp lignin were obtained from studies by Gellerstedt *et al.* (1988, 1994): an average oxygen content of 28.0 % for birch kraft lignin and 29.0 % for oxygen-delignified pulp lignin.

The applied oxygen contents of 48.9 % and 48.8 % for softwood and hardwood pulp carbohydrates, respectively, were obtained using the chemical compositions of cellulose and hemicelluloses and their proportions in the pulp (Alén, 2000b; Gullichsen, 2000). The formation of carboxyl structures into the polysaccharide chain during oxygen delignification was not taken into account, although they should add to the oxygen content of the pulp to some extent. Evidently this is not an important factor since, according to elemental analyses of pulp, the total oxygen content of pulp seems to stay practically unchanged during the delignification process.

The oxygen content of the different organic compounds dissolved in the liquor, apart from lignin, was calculated from their molecular structure. For dissolved carbohydrates the same factor was used as for the carbohydrates in pulp.

In addition to its consumption in the degradation and dissolution of lignin from pulp, oxygen is also consumed in the reactions with lignin in the liquor carried over from pulping. Studies reporting on the chemical composition of lignin also provided information on the oxygen content of dissolved softwood kraft lignin: on average 28.0 % oxygen was bound to the dissolved lignin before and 37.2 % after oxygen delignification (Gellerstedt and Lindfors, 1987; Sun and Argyropoulos, 1995). The actual oxygen content of lignin (37.2 % *vs.* 28.0 %) in the feed liquor depends on the assumption of how much lignin has already gone through the oxygen delignification process due to the counter-current filtrate circulation system. It is probable that most (~90 %) of the lignin in the effluent has been oxidized before entering the oxygen stage.

Information about the oxygen content of the oxygen-delignified birch lignin dissolved in the liquor was not readily available; therefore a value of 37.2 % was used, which had been defined for the corresponding softwood lignin. This was considered justified since in practice the oxygen content of softwood and that of birch pulp lignin were rather similar – for kraft/oxygen-delignified pulp lignin: 27.9 %/29.8 % (softwood) and 28.0 %/29.0 % (hardwood) – and it was thus reasonable to assume that the values for the dissolved lignin would also be similar.

Origin and consumption of oxygen

The fate of charged oxygen during delignification was determined by studying the chemical reactions between oxygen, alkali, and pulp components.

As lignin itself is diverse and has different functional groups, its reactions in oxygen delignification also proceed through various alternative routes. Although the main reaction mechanisms for lignin have been proposed, it remains impossible in practice to know exactly how much molecular oxygen is consumed in the oxidation of lignin structures, for example, in the formation of acidic groups. Further reactions resulting in the formation of aliphatic degradation products occur through the combined action of O_2 and HO^- (Young and Gierer, 1976; Gellerstedt and Lindfors, 1987). Nonetheless, few studies have attempted to approximate the oxygen consumed during the oxidation of lignin.

On the basis of the mechanisms governing the formation of some reaction products from lignin model compounds, it has been estimated that 0.25 - 1.5 oxygen molecules react with one aromatic ring unit in phenolic model compounds (Eckert *et al.*, 1973; Gierer and Imsgard, 1977b; Gierer *et al.*, 2001; Imai *et al.*, 2005). According to Tong *et al.* (2000, 2003), one lignin unit (C_6C_3) was found to be oxidized by about 3 electrons on average (delignification degree 50 %), when measured with permanganate oxidation. These data indicated that one aromatic unit in kraft lignin reacted with ~1 oxygen molecule on average; whereas the actual measurement of oxygen consumption during the oxygen-alkali treatment of lignin model compounds in a laboratory reactor has revealed that the aromatic ring unit present in kraft lignin consumes approximately 3 oxygen molecules (Imai *et al.*, 2005). However, in these experiments, the oxygen consumed was presumably also involved in the formation of small degradation products such as acids or CO_2 and not just in the oxidation of the aromatic ring. On the basis of the literature and proposed reaction paths (Gierer and Imsgard, 1977a) it was concluded that at least one oxygen molecule per phenylpropane unit is needed when lignin degrades or undergoes other structural conversions. Thus, the amount of oxygen consumed was obtained using the amount of lignin and the average molecular mass of one phenylpropane unit (185 g/mol) calculated from the elemental composition information in the study by Gellerstedt and Lindfors (1987).

Other, possibly molecular oxygen-consuming, lignin-related reactions are responsible for the formation of certain low-molecular-mass compounds, such as volatile and dicarboxylic acids, which are discussed below. The methoxyl groups of lignin were considered to be the main source of methanol and for this reason: the formation of methanol does not bind additional oxygen.

The main reaction products of carbohydrate degradation, hydroxy monocarboxylic acids, are formed as a result of different oxidative and alkaline peeling reactions. According to the proposed reaction mechanisms (Kolmodin and Samuelson, 1972; Malinen 1975) one oxygen in the molecular structure of these acids does not originate from the substrate, *i.e.*, it is added to the reaction product. The main reaction schemes (Figs. 5-6 and Appendix 1) also give a justification for roughly dividing the formation of hydroxy monocarboxylic acids into two groups: hydroxy acids formed as a result of the combined action of oxygen and alkali, and the acids considered to be formed due to the action of alkali alone.

Oxygen in volatile acids, on the other hand, was equally divided between oxygen from the pulp and oxygen from O_2/HO^-. Although, especially in the case of some carbohydrate reactions, the formation of volatile acids includes oxidation, other possible reaction routes may include degradation without any additional oxygen contributing to the reaction product, *i.e.,* both carboxylic oxygen molecules have their origin in pulp components. The estimation above was performed since there was no a way of determining the relative origin of these acids and no details were available in the literature.

The occurrence of inorganic carbonate in the filtrate arises from OWL and from the oxidation of organic material to carbon dioxide, which in alkaline conditions results in the formation of carbonate. It is probable that in the formation of carbon dioxide, part of the oxygen originates from the degrading material and part from molecular oxygen. Since one oxygen atom in carbonate originates from HO^-, the oxygen content in CO_3^{2-} could be divided according to its origin: organic material/molecular oxygen and alkali. The minimum amount of oxygen in carbonate originating from molecular oxygen can be estimated by dividing the origin of oxygen equally between molecular oxygen, alkali, and pulp, although some reaction schemes propose that degradation of aromatic ring in lignin can result in CO_2 formation. Thus, CO_2 formation would not bind any additional oxygen. In calculating the maximum amount it would have to be assumed that both of the oxygen atoms in CO_2 originate from molecular oxygen.

If OWL containing residual Na_2S is used in the process, considerable amounts of oxygen can be consumed in the oxidation reactions of sulfur. According to the reactions (1-4), half of the oxygen in the end product sulfate, originates from molecular oxygen and the other half from alkali and thiosulfate.

$$2\,NaHS + 2\,O_2 \rightarrow Na_2S_2O_3 + H_2O \qquad (1)$$

$$2\,Na_2S + 2\,O_2 + H_2O \rightarrow Na_2S_2O_3 + 2\,NaOH \qquad (2)$$

$$Na_2S_2O_3 + O_2 + 2\,NaOH \rightarrow 2\,Na_2SO_3 + H_2O \qquad (3)$$

$$2\,Na_2SO_3 + O_2 \rightarrow 2\,Na_2SO_4 \qquad (4)$$

3.3.2 Yield and selectivity

Yield

The loss in yield, *i.e.,* loss of pulp material, is due to lignin and carbohydrate removal. As mentioned earlier, the soluble pulp-derived components formed during oxygen delignification could be a measure of yield loss. As a part of this study, three different methods of estimating pulp yield in an oxygen delignification process were used.

The first method (Yield I) was based simply on the increase in dissolved solids (DS) during oxygen delignification. In the case of softwood, the effect of alkali had to be excluded from the analytical results by calculatory means. Dissolved solids content (DS_{alkali}) in the added alkali (OWL and fresh NaOH) was excluded from the yield calculation.

Yield loss I (kg/BDt) = ΔDS

For softwood: Yield loss I (kg/BDt) = $\Delta DS - DS_{alkali}$

$\Delta DS = DS_{Blow} - DS_{Feed}$

Yield I (%) = 100 - 0.1 * Yield loss I

The second method (Yield II) was based on the carbon material balance. The increases in TOC and TIC in the liquors were taken into account. Again the effect of OWL (TIC_{OWL}) was excluded from the softwood results. When building a link between the amount of carbon in the liquors and pulp yield, an estimation of the carbon content of the dissolved pulp material was needed. A good approximation for this was based on the 50/50 material loss assumption for lignin and carbohydrates in softwood kraft pulp (Malinen, 1975; Lai et al. 1994). Thus, mean carbon content in the dissolved wood material was approximately 54 %, *i.e.,* midway between 64 % carbon in kraft lignin (Gellerstedt and Lindfors, 1987) and 45 % in initial carbohydrates (Alén, 2000b).

Yield loss II (kg/BDt) = $(\Delta TOC + \Delta TIC)/0.54$

For softwood: Yield loss II (kg/BDt) = $(\Delta TOC + \Delta TIC - TIC_{OWL})/0.54$

$\Delta TOC + \Delta TIC = (TOC_{Blow} - TOC_{Feed}) + (TIC_{Blow} - TIC_{Feed})$

Yield II (%) = 100 - 0.1 * Yield loss II

The third method (Yield III) summarized the amounts of the individual components formed as dissolved reaction products (DP) during the oxygen delignification process. Such components were lignin, carbohydrates, methanol, formic and acetic acids, hydroxy acids, and TIC. TIC_{OWL} was excluded from the sum of softwood components.

Yield loss III (kg/BDt) = ΔDP

For softwood: Yield loss III (kg/BDt) = $\Delta DP - TIC_{OWL}$

$\Delta DP = DP_{Blow} - DP_{Feed}$

Yield III (%) = 100 - 0.1 * Yield loss III

Selectivity

The selectivity of a pulping or a bleaching process can be defined in several different ways as mentioned in the Introduction section. The methods described here attempt to estimate the selectivity of oxygen delignification mainly by means of dissolved components.

The first method (Selectivity 1) corresponded to the ratio of soluble lignin fragments (as carbon) to the increase in dissolved carbon during delignification. The amount of carbon in the released lignin was estimated using the correlation between kappa number and lignin content and the carbon content in lignin. The relation between kappa and lignin in pine kraft pulp (Alén and Sjöström, 1991) was

$$\text{kappa number} = 6.67 * [(\text{lignin-}\%) + 0.13]$$

and in birch kraft pulp (Kyrklund and Strandell, 1969; Gullichsen, 2000)

$$\text{kappa number} = 6.064 * \text{lignin-}\%.$$

The carbon content of softwood lignin was 64 % (Gellerstedt and Lindfors, 1987) and 63 % that of hardwood kraft lignin (Gellerstedt *et al.*, 1988, 1994). The effect of HexAs was excluded from the original kappa number to obtain a "modified kappa number" more accurately representing the actual amount of lignin (10 mmol of HexAs corresponds to 0.86 kappa units) (Li and Gellerstedt, 1997), since the traditional kappa number does not correspond to the actual amount of lignin present in the pulp (Chapter 2.3.2). Thus, Selectivity 1 was calculated as the ratio between the carbon content of the released lignin in the pulp on the amount of carbon in all reaction products. TIC content in the added alkali was excluded from the softwood balances.

For softwood delignification:

$$\text{Selectivity 1 (\%)} = 100 * [(10 * (\Delta\text{mod. kappa}/6.67-0.13) * 0.64)/(\Delta\text{TOC} + \Delta\text{TIC} - \text{TIC}_{\text{OWL}})]$$

For hardwood delignification:

$$\text{Selectivity 1 (\%)} = 100 * [(10 * (\Delta\text{mod. kappa}/6.064) * 0.63)/(\Delta\text{TOC} + \Delta\text{TIC})]$$

In the second method (Selectivity 2) the released lignin (kg/BDt) was related to the total amount of reaction products formed in this process. The amount of decreased lignin in pulp was estimated according to Selectivity 1. The total amount of reaction products (DP) was calculated as the sum of all the reaction products measured (lignin, carbohydrates, methanol, formic and acetic acid, hydroxy acids, TIC). The effect of added alkali on TIC was again excluded from the softwood balances.

For softwood delignification:

Selectivity 2 (%) = 100 * [10*(Δmod. kappa/6.67-0.13)/(ΔDP - TIC_{OWL})]

For hardwood delignification:

Selectivity 2 (%) = 100 * [10*(Δmod. kappa/6.064)/ΔDP]

The third method (Selectivity 3) was based on lignin-derived reaction products dissolved during delignification. On the basis of earlier studies (see chapter 2.3.4 "Reaction products") it was assumed that dicarboxylic acids, methanol, and most of the carbon dioxide (70 %), in addition to dissolved lignin fragments, derived from kraft lignin. Half of the contents of formic and acetic acid were also added to the sum of the above mentioned components, on the grounds that they could be categorized as equally likely lignin- and carbohydrate-derived reaction products. Thus, Selectivity 3 was calculated as the ratio between the assumed amount of lignin-derived reaction products (DP_{lignin}) and the total amount of reaction products.

For softwood delignification:

Selectivity 3 (%) = 100 * [ΔDP_{lignin} / (ΔDP - TIC_{OWL})]

For hardwood delignification:

Selectivity 3 (%) = 100 * (ΔDP_{lignin} / ΔDP)

$\Delta DP_{lignin} = DP_{lignin,\ blow} - DP_{lignin,\ feed}$

In the fourth method (Selectivity 4), the amounts of specific carbohydrate-derived hydroxy acids (2-hydroxybutanoic, 3,4-dihydroxybutanoic, 2,4-dihydroxybutanoic, 3-deoxytetronic, 3-deoxypentonic, xyloisosaccharinic, and glucoisosaccharinic acids) and dissolved carbohydrates ($DP_{carboh.}$) were related to lignin removal from the fibers.

For softwood delignification:

Selectivity 4 (%) = 100 * {1-k [ΔDP_{carboh} /(10*(Δmod. kappa/6.67-0.13))]}

For hardwood delignification:

Selectivity 4 (%) = 100 * {1-k [ΔDP_{carboh} /(10*(Δmod. kappa/6.064))]}

$\Delta DP_{carboh.} = DP_{carboh.,\ blow} - DP_{carboh.,\ feed}$

K = constant = 1

Selectivity 5 represented the traditional way of expressing selectivity in connection with oxygen delignification. Thus, it was calculated as the ratio between the reduction in pulp viscosity and the degree of delignification. In contrast to the earlier methods, the degree of delignification in Selectivity 5 was estimated directly from the original kappa number of the pulps, *i.e.* ithout any correction for HexAs. This was done for the purpose of comparing, in as simple manner as possible, the traditional method of selectivity with the other methods.

$$\text{Selectivity 5 } (\%) = 100 - k * (\Delta\text{viscosity}/\Delta\text{kappa number})$$

$$K = \text{constant} = 1$$

4 RESULTS AND DISCUSSION

4.1 Material balances

4.1.1 Softwood and hardwood delignification

Material balances (in the amount of kg/BDt) for the oxygen stage were calculated from the analytical data and the amount of liquor (Tables 10-13). The total amount of liquor carried with the pulp feed to the oxygen delignification process was calculated using an average of two measured consistencies (feed and blow). The amount of liquor carried with the pulp blown out of the softwood oxygen delignification process was calculated to be 0.12-0.21 m^3/BDt higher than the amount of liquor in the pulp feed. This estimation was made in order to decrease possible errors in the individual consistency measurements, and to cover the systematic effect of steam and alkali additions to the softwood system. The quantity of carbonate in the filtrates was calculated from the content of TIC. The addition of inorganic ions ($S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, and CO_3^{2-}) to softwood liquor was estimated according to the sodium balance, the OWL charge, and results of the OWL analysis. Alkali and liquor corrections were not needed in the case of hardwood material balances. The analytical results of the hardwood trials were average values of the two individual samples taken at the sampling sites during each run. The average relative standard deviation for the analysis results of these two samples was between 2.0-3.7 %.

As expected, the test runs showed differences in delignification responses due to varying process conditions. The degree of delignification for softwood pulps was 30-50 % (Δmod.kappa 7.0-10.5) and for birch pulps 38-46 % (Δmod.kappa 5.4-6.6), the most effective lignin removal taking place during Runs 4 (softwood) and 2 (hardwood). The trials with highest oxygen charges showed the greatest decrease in kappa number and viscosity.

The increase in the amount of hexenuronic acids during oxygen delignification of softwood pulp may partly be explained by the experimental error (~5 %) of the method (Tenkanen *et al.* 1999). Also some other components dissolved from pulp may interfere at least at low concentrations (<1 mmol/kg) of HexAs. As mentioned earlier, there has also been an indication that HexAs might be formed during oxygen delignification (Antonsson *et al.* 2003).

Oxygen delignification of softwood pulp resulted in the formation of 15-26 kg/BDt of reaction products and in the hardwood case in 18-24 kg/BDt (Tables 11 and 13). Dissolved lignin fragments accounted for 57-62 % and acids for 17-26 % of the total analyzed components in softwood liquor. Together lignin and hydroxy acids comprised 61-70 % of the hardwood reaction products. In addition, considerable amounts of volatile acids were formed, in general more from hardwood pulp than from softwood pulp. In contrast, the amounts of dissolved carbohydrates (5-10 %), which were mainly hemicelluloses, and methanol hardly exceeded 2 kg/BDt. The low amount of carbohydrates in liquor indicated extensive degradation of dissolved polysaccharide fragments.

TABLE 10 Analytical data[1] on the softwood pulps and filtrates (I; II; III)

Characteristic	Unit	Run 1		Run 2		Run 3		Run 4	
		Feed	Blow	Feed	Blow	Feed	Blow	Feed	Blow
Pulp									
Consistency	%	10.1	11.8	10.0	10.7	10.2	10.9	9.9	10.9
Kappa		28.9	18.7	26.0	18.5	22.6	15.7	22.3	12.0
HexA	mmol/kg	19.1	21.3	13.4	14.3	16.2	18.0	15.7	18.1
Mod. Kappa[2]		27.3	16.9	24.8	17.3	21.2	14.2	20.9	10.4
Viscosity	cm^3/g	1140	1020	985	910	1050	955	1065	880
C	%	-	-	-	-	43.7	43.6	43.7	43.8
H	%	-	-	-	-	6.2	6.4	6.3	6.2
N	%	-	-	-	-	< 0.1	0.1	0.1	< 0.1
Filtrate	mg/dm^3								
Dissolved solids		18000	24100	14400	18400	20200	24900	19700	24700
Sodium		3900	5800	3310	4310	4600	5700	4500	5500
TOC		3920	5010	3010	3720	4690	5420	4270	5560
TIC		540	760	330	520	520	620	460	660
Lignin		3810	5550	2400	3420	4430	5650	4210	5630
Carbohydrates		1290	1570	1200	1350	840	920	700	890
Methanol		530	620	460	510	360	550	480	540
Formic acid		630	870	510	610	670	790	630	840
Acetic acid		300	360	240	270	230	260	220	260
Hydroxy acids		1210	1520	1070	1200	1630	1860	1570	1970
$S_2O_3^{2-}$		-	-	-	-	400	720	310	210
SO_3^{2-}		-	-	-	-	90	110	80	0
SO_4^{2-}		-	-	-	-	28000	3400	2900	4000
OWL	g/dm^3								
Na_2S		-		-		7.6		6.4	
$S_2O_3^{2-}$		-		-		41.9		37.8	
SO_3^{2-}		-		-		5.5		7.1	
SO_4^{2-}		-		-		19.9		27.2	

[1] Average relative standard deviation (RSD) between replicate analyses was 2.9 %

[2] Modified kappa corrected for HexAs (kappa unit = 11.6 mmol HexA/kg o.d. pulp)

TABLE 11 Component material balances: softwood oxygen delignification (kg/BDt) (I; II; III)

Characteristic	Run 1			Run 2			Run 3			Run 4		
	Feed	Blow	Δ	Feed	Blow	Δ	Feed	Blow	Δ	Feed	Blow	Δ
Amount of liquor (m^3 / BDt)	8.13	8.31	0.18	8.66	8.78	0.12	8.48	8.69	0.21	8.6	8.8	0.2
Dissolved solids[1]	146.3	200.3	54.0	124.7	161.6	36.9	171.3	216.4	45.1	169.8	217.9	48.1
Sodium	31.7	48.2	16.5	28.7	37.8	9.1	39.0	49.5	10.5	38.8	48.5	9.7
TOC	31.9	41.7	9.8	26.1	32.7	6.6	39.7	47.1	7.3	36.8	49.0	12.2
TIC[2]	4.4	6.3	1.9	2.9	4.6	1.7	4.4	5.4	1.0	3.9	5.8	1.9
Lignin	31.0	46.1	15.1	20.8	30.0	9.2	37.6	49.1	11.5	36.3	49.6	13.3
Carbohydrates	10.5	13.0	2.5	10.4	11.9	1.5	7.1	8.0	0.9	6.0	7.8	1.8
Methanol	4.3	5.2	0.9	3.9	4.5	0.6	3.1	4.8	1.7	4.1	4.7	0.6
Formic acid	5.1	7.2	2.1	4.4	5.4	1.0	5.7	6.9	1.2	5.5	7.4	1.9
Acetic acid	2.4	3.0	0.6	2.1	2.4	0.3	1.9	2.3	0.4	1.9	2.3	0.4
Hydroxy acids	9.8	12.6	2.8	9.3	10.5	1.3	13.8	16.2	2.4	13.5	17.4	3.9
Monocarboxylic	7.2	8.9	1.7	7.2	8.0	0.8	11.0	12.6	1.6	10.6	13.2	2.6
Dicarboxylic	2.6	3.7	1.1	2.1	2.5	0.4	2.9	3.6	0.7	3.0	4.2	1.2
Sulfur ions (total)			-			-			3.0			2.4

[1]Amount (kg/BDt) from alkali charge 35.5, 23.9, 26.6, and 24.7 in Runs, respectively
[2]Amount (kg/BDt) from alkali charge 0.29, 0.30, 0.24, and 0.23 in Runs, respectively

TABLE 12 Analytical data[1] on the hardwood pulps and filtrates (IV). Numbers are average values of the two individual samples taken at each site

Characteristic	Unit	Run 1		Run 2		Run 3	
		Feed	Blow	Feed	Blow	Feed	Blow
Pulp samples							
Consistency	%	9.7	9.8	9.4	8.9	9.1	9.0
Kappa number		16.6	11.1	17.5	10.9	19.3	13.4
HexAs	mmol/kg	39.2	38.8	39.2	38.3	40.8	41.9
Mod. kappa		13.2	7.8	14.2	7.6	15.8	9.8
Viscosity	cm^3/g	1290	1060	1240	990	1290	1090
Filtrate samples	mg/dm^3						
Dissolved solids		18850	20700	30150	33050	37450	40300
Sodium		5300	5300	8200	8400	10700	10800
TOC		3050	4010	4240	5220	5490	6530
TIC		560	670	820	1000	880	1000
Lignin		2750	3500	3800	4650	4700	5760
Carbohydrates		990	1190	1030	1180	1110	1170
Methanol		390	510	360	510	460	560
Formic acid		650	890	840	1180	1030	1360
Acetic acid		240	350	330	390	400	460
Hydroxy acids		1450	1910	2030	2720	2370	2800
$S_2O_3^{2-}$		640	20	1385	270	2995	2155
SO_3^{2-}		0	0	340	135	380	275
SO_4^{2-},		2850	3850	5450	7050	5800	7000
pH		-	-	12.7	10.8	13.1	12.8
OWL	g/dm^3						
Na_2S		0.49		11.3		4.4	
$S_2O_3^{2-}$		53.1		43.2		51.1	
SO_3^{2-}		0		0		1.6	
SO_4^{2-}		8.9		13.1		12.5	

[1]Average relative standard deviation (RSD) between replicate analyses was 2.8 % and between analytical results of the two individual samples 5.3 %

TABLE 13 Component material balances: hardwood oxygen delignification (kg/BDt) (IV)

Characteristic	Run 1			Run 2			Run 3		
	Feed	Blow	Δ	Feed	Blow	Δ	Feed	Blow	Δ
Amount of liquor (m^3 / BDt)	9.3	9.3	0.0	10.0	10.0	0.0	10.1	10.1	0.0
Dissolved solids	174.5	191.6	17.1	301.5	330.5	29.1	378.3	407.0	28.7
Sodium	49.3	49.3	0.0	82.0	84.0	2.0	107.5	108.5	1.0
TOC	28.2	37.1	8.9	42.3	52.1	9.8	55.2	65.6	10.4
TIC	5.2	6.2	1.0	8.2	10.0	1.8	8.9	10.0	1.1
Lignin	25.4	32.4	7.0	38.0	46.5	8.5	47.3	57.9	10.6
Carbohydrates	9.1	11.0	1.9	10.3	11.8	1.5	11.1	11.7	0.6
Methanol	3.6	4.7	1.1	3.6	5.1	1.5	4.6	5.6	1.0
Formic acid	6.0	8.3	2.2	8.4	11.8	3.4	10.3	13.6	3.3
Acetic acid	2.2	3.3	1.1	3.3	3.9	0.6	4.0	4.6	0.6
Hydroxy acids	13.4	17.7	4.3	20.3	27.2	6.9	23.9	28.3	4.4
Monocarboxylic	11.6	15.1	3.5	17.6	23.5	5.9	20.9	24.7	3.8
Dicarboxylic	1.8	2.6	0.8	2.7	3.6	0.9	2.9	3.5	0.6
Sulfur ions (total)			3.3			3.0			2.5

The amounts of reaction products and the degree of delignification according to kappa number, especially in hardwood Run 1, were in line with the findings of Ristolainen and Alén (1998) who reported the amounts of carbohydrates, lignin and carboxylic acids dissolved in the oxygen stage effluent to be 2.5, 6.4 and 3.3 kg/BDt (Δkappa 5.5, delignification degree 33 %). The composition of the acids in the liquor was also consistent with earlier reported, formic, acetic, and glycolic acids being the most abundant (Pfister and Sjöström, 1979; Ristolainen and Alén, 1998). Oxalic acid and 2-deoxy-tetronic acid, the latter of which is a characteristic product of cellulose and glucomannan degradation, were also detected in considerable amounts in softwood liquors. Typical acids deriving from xylan are 3-hydroxypropanoic and 3-deoxy-tetronic, which were among the most abundant acids in the hardwood effluents.

Oxalic acid in softwood samples 1 and 2 was determined by GC and hence most likely, the results underestimate the true amounts formed. When the results obtained by GC and IC analysis for samples 3 and 4 were compared, it could be seen that approximately half of the oxalic acid was lost during the GC determination. Although the use of GC results for oxalic acid has a marked effect on the relative acid composition, the error caused to the total amount of components was only 1-3 %.

When additional inorganic carbon was converted to carbonate, on the assumption that it all derived from the formation of carbon dioxide, carbonate was the main individual component in the liquor besides lignin totaling 4-9 kg/BDt. A high amount of carbon dioxide has been observed previously (7.49 kg/t pulp) (Pfister and Sjöström, 1979), and the present results were also very similar to those obtained by Chai *et al.* (2003a) who measured the amount of carbonate formed during oxygen delignification being approximately 0.40 g/dm^3 and 0.89 g/ dm^3 at Δkappa 7.1 and 10.5, respectively. This corresponded to softwood trials 3 (Δkappa 6.9) and 4 (Δkappa 10.3), where carbonate accounted for 0.47 g/ dm^3 and 0.95 g/ dm^3, respectively. The results were also on the same level with those obtained from laboratory oxygen delignification (Fu *et al.*, 2004) where carbonate formation was around 80 µmol/g pulp (final kappa number ~10), corresponding to 4.8 kg/t of pulp.

It is clear that there are differences between the trials with different process conditions but it is difficult to define whether this is a result of oxygen or alkali or simply because delignification is subjected to more "effort" by either of these chemicals. Nonetheless, the results suggested some relationships between the main reaction products and the process parameters (*i.e.*, the charged OWL and oxygen). The double amount of oxygen charged in softwood Run 4 as well as the higher alkali in Run 1, compared to the other softwood trials, could both be seen in a higher amount of dissolved reaction products. The amount of dissolved hardwood lignin correlated well with the OWL charged. The charged oxygen appeared in the fraction of hydroxy acids as a result of the increase in oxidative reactions. Further oxidative degradation was also evident from the significant formation of carbonate. The sulfur ions ($S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-}) originating from OWL constituted 9-19 % of the dissolved solids, corresponding to about 3 kg/BDt in the balances.

When comparing the material balances of the softwood and birch kraft pulps (Fig. 9), it was found that they differed, especially in the amounts of hydroxy monocarboxylic acids and volatile acids, as well as in the amount of lignin. More aliphatic acids were formed and less lignin dissolved during the oxygen delignification of birch kraft pulp than of softwood kraft pulp. The extent of the degradative peeling reaction of xylan has been observed to be greater then that of cellulose or glucomannans (Malinen, 1974) and the more drastic oxidative depolymerization of xylan compared to cellulose is possibly due to physical factors such as solubility and accessibility. It has also been reported before that hardwood kraft pulps are less responsive to oxygen delignification than softwood pulps (Shin *et al.*, 2006). One reason for this may be the structural differences between hardwood and softwood lignin: the residual lignin in most hardwood pulps has a lower phenolic hydroxyl group content than that of the softwood pulps. This might contribute to poorer performance of hardwood pulps since hydroxyl groups are important reactive sites in oxygen delignification.

The nature of the residual lignin and LCCs in kraft pulp should also be considered. As suggested by Lawoko et al. (2003) most of the residual lignin in kraft pulp is chemically bonded to hemicelluloses. A further observation has been that different kinds of LCC have different reactivity during delignification (Lawoko et al. 2004). One hypothesis is that the higher solubility of xylan compared to glucomannan under alkaline conditions may expose the bound lignin to the delignifying chemicals. This would also mean that the xylan is more prone to attack from hydroxyl radicals and thus degradation.

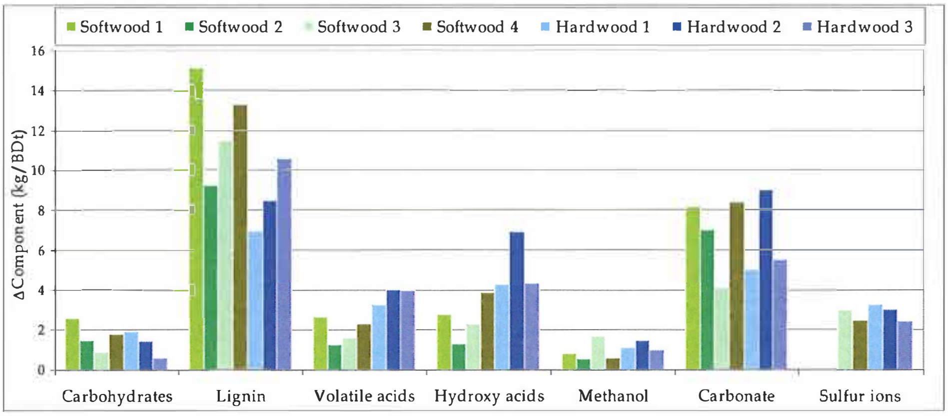


FIGURE 9 Comparison of the increased amounts of the dissolved reaction products of softwood and hardwood.

However, it must also be taken into account that these oxygen-alkali processes were significantly different: softwood delignification was performed as a two-stage and birch delignification as a single-stage process, and the OWL used in the softwood process was prepared with molecular oxygen. The difference in degree of delignification between one-and two-stage systems has been reported to be 5-6 % in favor of two-stage oxygen delignification (Carter *et al.*, 1997). Kraft cooking conditions have also been noticed to affect oxygen delignification performance (Chen *et al.*, 1995).

4.1.2 Bamboo delignification

The bamboo pulps differed from wood pulps in the sense that they were cooked and delignified on a laboratory scale. For this reason, examination of the pulping process and its effect on the oxygen delignification were also included in the results.

The delignification conditions for both bamboo cooking experiments were identical except for the alkali charge (EA 14 % or 20 %), which resulted in clear differences in kappa number and viscosity values (Table 14) as well as in the chemical composition of the pulps (*i.e.*, kraft pulp 1 and kraft pulp 2, respectively) and black liquors (*i.e.*, BL 1 and BL 2, respectively) (Table 15). The total cooking yields (50.4 % and 47.7 %, for the cooks with EA 14 % or 20 %, respectively) were similar to those obtained earlier from this non-wood raw material under the same conditions (Vu, 2004).

TABLE 14 Some characteristics of the bamboo pulps[1] (V)

Characteristic	Unit	Kraft Pulp 1	O_2-pulp 1	Δ	Kraft Pulp 2	O_2-pulp 2	Δ
Yield	%	50.4	97.5		47.7	98.1	
Kappa number		20.0	11.5	-8.5 (-42.5 %)	13.6	6.9	-6.7 (-49.3 %)
Mod. kappa		19.1	10.8	-8.3 (-43.5 %)	12.9	6.3	-6.6 (-51.2 %)
Viscosity	cm^3/g	1310	1040	-270 (-20.6 %)	1160	940	-220 (-19.0 %)
Extractives	g/kg	2.9	1.8	-1.1	2.5	1.5	-1.0
HexA	mmol/kg	10.7	8.6	-2.1	8.6	6.8	-1.8
-COOH	meq./kg	105	105	±0	95	92	-3
C	%	39.8	39.5	-0.3	39.0	39.4	0.4
H	%	6.3	6.3	±0	6.2	6.3	0.1
N	%	-	-	-	-	-	-
S	%	0.05	0.03	-0.02	0.04	0.02	-0.02
O[2]	%	53.54	53.85	0.31	54.51	53.98	-0.53
Si	%	0.07	0.05	-0.02	0.06	0.05	-0.01
Metals[3]	%	0.24	0.24	±0	0.19	0.20	0.01

[1] Pulps 1 and 2 from cooking with EA 14 % and 20 %, respectively

[2] Calculated as a difference: 100 % - (C+H+S+Si+metals)

[3] Include the analyzed metals: Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, and Zn. The increase in magnesium due to $MgSO_4$ addition is excluded from the O_2-pulps

The decrease in kappa number during oxygen delignification was 42-49 % and in viscosity 19-21 %. In addition, the content of extractives decreased somewhat, although no clear effect on the elemental composition of pulp was detected. The oxygen delignification response was better in pulp 2, which was cooked in higher alkali conditions. This result that a high alkali charge or sulfidity in kraft cooking increases the reactivity of pulp lignin has been reported earlier (Pekkala, 1984; Pu *et al.*, 2002).

Other cooking experiments (not reported in detail here) performed with the same laboratory-scale digester under similar conditions have indicated average total yields for wood pulps (spruce, birch, and aspen pulps) of 42-53 %. The kappa numbers and the viscosity values of these kraft pulps were in the range 16-29 and 1200-1370 cm^3/g, respectively, the outcome of birch pulping most resembling that of the bamboo pulps. All these data suggest that, compared to wood-based raw materials, bamboo can be delignified rather easily, as has also been shown elsewhere (Gomide *et al.*, 1991; Vu, 2004). In addition, the relationship between the kappa number and viscosity of bamboo kraft pulps has been found (Vu, 2004) to resemble that for wood-based rather than typical non-wood kraft pulps.

Since HexAs do not react under oxygen delignification conditions, the loss in the amount of HexAs in pulp was probably due to the conversion of xylan into soluble fragments. The amount of HexAs was substantially lower in bamboo pulps (8.6-10.7 mmol/kg) than in hardwood pulps (38-76 mmol/kg (Li and Gellerstedt, 1997; Evtuguin *et al.*, 2000; Jiang *et al.*, 2000) or in softwood pulps (16-23 mmol/kg (Allison *et al.*, 1999; Toven and Gellerstedt, 1999) at approximately the same kappa number level.

It is noteworthy that the total amount of carboxylic acid groups remained rather constant (around 100 mmol/kg) during delignification in spite of the decrease in the amount of HexA groups. It is known (Alén, 2000a) that the stopping reactions of carbohydrates introduce new carboxylic acid groups into pulp and that some lignin reactions may also lead to the formation of new carboxylic groups (Sun and Argyropoulos, 1995; Jiang and Argyropoulos, 1999). In our case, less than about 10 % of the carboxylic groups in the kraft pulps (kraft pulp 1 and 2) and oxygen-delignified pulps (O_2-pulp 1 and 2) derived from HexAs. However, part of the total amount of carboxylic groups was also due to the presence of other uronic acid groups, such as those of 4-*O*-methylglucoronic acid, 4-*O*-methyliduronic acid, galacturonic acid and glucuronic acid, which were not separately determined in this study. In general, the total amount of carboxylic acid groups in bamboo pulps is similar to that in hardwood kraft pulps (Evstigneyev *et al.*, 2003), although the total amount of HexA groups is clearly lower.

TABLE 15 Chemical composition (mg/dm^3) of the black liquors (BLs) and oxygen delignification filtrates (O_2-filtrates) of bamboo

Characteristic	BL 1	BL 2	O_2- filtrate 1	O_2- filtrate 2
Dissolved solids	151000	168000	6000	5100
TOC	57100	67600	2080	1300
IC	1040	1360	170	150
Lignin	58200	61400	1440	910
Carbohydrates	3585	3010	455	235
Methanol	430	510	110	80
Volatile acids	10420	12040	280	230
Hydroxy acids	16900	19770	675	760
monocarboxylic	15830	18300	595	700
dicarboxylic	1070	1470	80	60

As expected, in the case of a higher EA more organic material was dissolved during delignification in the black liquor than in case of a lower EA (Table 15). This could also be seen in the total amounts of aliphatic carboxylic acids, although no significant differences in the relative compositions of these acids between the black liquors were detected. In addition, the total amount of soluble carboxylic acids (10.9-12.7 % of raw material) was consistent with that found in previous studies: 12-15 % (Feng *et al.*, 2002) and 11-15 % (Vu *et al.*, 2003). The relative composition of these acids resembles those found in black liquor of birch kraft pulp. For example, the formation of 2-hydroxybutanoic, xyloisosaccharinic, and glucoisosaccharinic acids in the pulping of birch and bamboo is alike, clearly differing from the lower level of acid formation obtained in softwood pulping.

The concentration of aliphatic carboxylic monoacids (volatile acids plus hydroxy monocarboxylic acids) in the effluents (*cf.* O_2-filtrate 1 *vs.* O_2-filtrate 2) was somewhat higher in the case of O_2-filtrate 2. The probable reason for this was the more severe delignification treatment in the second cook, which resulted in a carbohydrate matrix which was more reactive to alkaline peeling in the subsequent alkaline oxygen stage. In spite of this, no significant differences between O_2-effluent 1 and O_2-effluent 2 in the relative composition of these acids were detected. The most abundant acids were, in addition to formic acid, glycolic, 3-hydroxypropanoic, 2,4-dihydroxybutanoic, and 3-deoxy-pentonic acids, which are typical degradation products formed during oxygen delignification. As in the case of hardwood kraft pulp, the high amounts of 3-hydroxypropanoic and 2,4-dihydroxybutanoic acids indicated the intensive degradation of xylan, the major hemicellulose constituent in bamboo. As in the case of the black liquor the overall composition of hydroxy acids in the oxygen delignification effluent of bamboo also resembled that in hardwood effluents (Fig. 10), whereas the difference between the bamboo and softwood effluents was not as distinct as the difference between their black liquors.

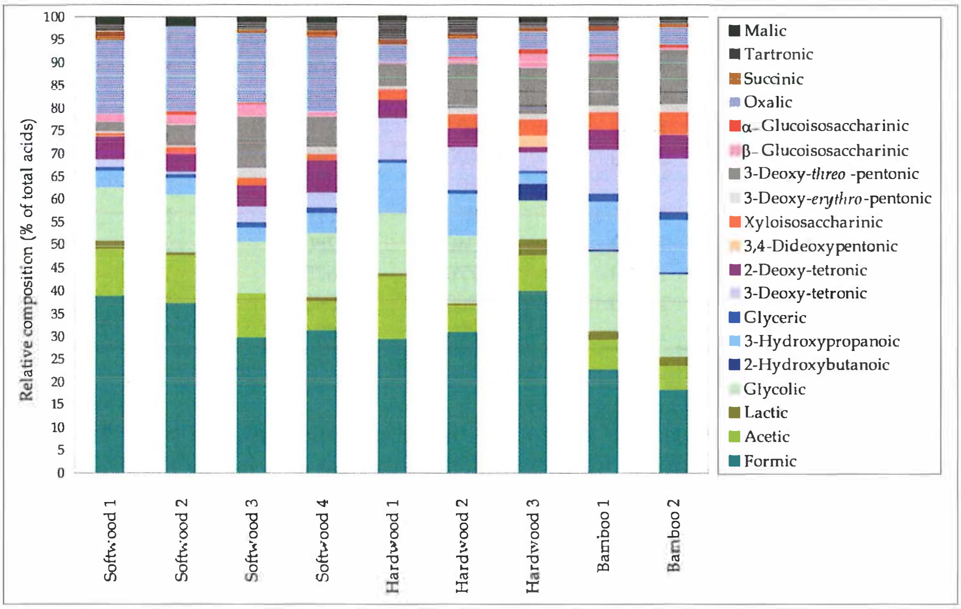


FIGURE 10 Proportions of total acids formed during oxygen delignification of softwood, hardwood, and bamboo.

4.2 Fate of oxygen

4.2.1 Softwood and hardwood delignification

Oxygen in reaction products

The estimations of bound oxygen (Fig. 11) for softwood experiments 3 and 4 (III) and hardwood (IV) show that the total mass-based proportion of oxygen in the dissolved organic components for softwood in Run 3 was 7.9 - 11.3 kg/BDt, which was similar to that found in the hardwood experiments (8.7-11.3 kg/BDt). In Run 4 amount of oxygen in organics was 10.1-13.5 kg/BDt.

The increase in oxygen in the liquor as part of the dissolved reaction products was 13.1-16.5 kg/BDt and 18.8-22.2 kg/BDt for softwood trials 3 and 4, respectively. The range in these figures is caused by the calculatory oxidation state of lignin (37.2 % *vs.* 28.0 %) – the minimum amount of oxygen presents a state where all the dissolved lignin entering the oxygen stage contains 37.2 % oxygen. For hardwood estimations the lignin oxidation state was assumed to be 37.2 %, both to simplify the results and since it most likely is closer to the real value. The total oxygen content in dissolved hardwood compounds comprised 16-23 kg of oxygen per BDt, the lowest amount occurring in Run 1 and largest in Run 2.

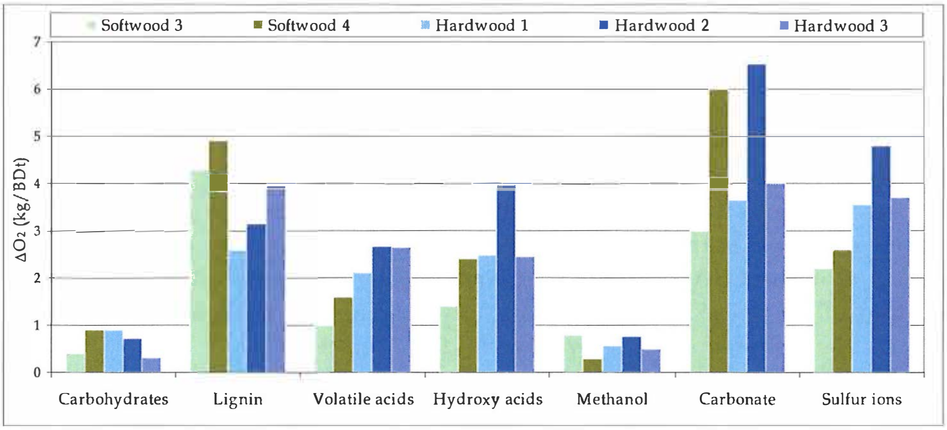


FIGURE 11 Comparison of the amount of oxygen in the dissolved reaction products of softwood and hardwood.

As a main individual reaction product, in addition to lignin, carbonate also had significant oxygen content (3-6 kg/BDt) compared to that of the other liquor components. Together carbonate and lignin contained 39-58% of the total oxygen in the analyzed components. When comparing, for example, the amount of oxygen bound to dissolved softwood lignin (Run 3 and 4) to the amount of charged oxygen, an increased the charge does not seem to lead to more oxidized and, subsequently, to more soluble lignin, as also detected by Sun and Argyropoulos (1995).

On the other hand, the effect of high oxygen charge was seen in hydroxy acid and carbonate formation during hardwood trial 2, as mentioned earlier. Also high alkali, and more importantly, high Na_2S concentration in the case of hardwood, resulted in considerable oxygen consumption on behalf of the sulfate formation.

Origin and consumption

Part of the total oxygen increase derived from the dissolving pulp components (yield loss). When deducting the decreased amount of oxygen in the pulp from the amount in the liquor, the total amount of oxygen added to the dissolving components was as follows: 7.1-10.5 kg/BDt for Run 3 and 10.5-13.9 kg/BDt for Run 4 and 8.1-12.8 kg/BDt for hardwood trials. According to the elemental analysis, total oxygen content of pulp seemed to stay practically unchanged during the delignification process. When the oxygen in pulp was calculated by subtracting the percentages of the other elements from 100 %, the difference between the feed and blow samples in oxygen content was no more than 0.1 % (*i.e.*, within the limits of accuracy). Lignin oxidation in pulp accounted for 0.2-0.4 kg oxygen per BDt (Appendix 4). Degradation and dissolving reactions of lignin on the other hand was estimated to use 1-2 kg oxygen/BDt calculated on the basis of dissolved phenolic lignin fragments.

Acids showed the widest distribution when trying to determine molecular oxygen consumption during their formation. For the reasons discussed in chapter 3.3.2, molecular oxygen bound to volatile acids could be something between 0-0.8 and 0-1.4 kg/BDt for softwood and hardwood reaction products, respectively. The variation in hydroxy acids was 0-0.9 kg/BDt.

According to the reaction equation (chapter 3.3.1) and the amount of SO_4^{2-} formed, oxidation of thiosulfate to sulfate in the softwood stage involved 1.4-2.6 kg/BDt molecular oxygen. Due to the notably larger concentrations of sulfide and thiosulfate in the hardwood than softwood liquors, the amount of oxygen consumed in sulfate formation was twofold (3.0-5.4 kg/BDt).

The maximum amount of molecular oxygen that can be consumed in the reactions is equal to the amount of O_2 gas charged. Thus, 8.8 kg/BDt and 17.8 kg/BDt were the upper limits for oxygen consumption in softwood Runs 3 and 4, and 6.1/17.7/12.3 kg/BDt in hardwood Runs 1/2/3, respectively. Estimations indicated that the amount of molecular oxygen needed for the reactions in softwood process was only 39-68 % of the charge: 4 - 6 kg/BDt in Run 3 and 7-10 kg/BDt in Run 4 (Fig. 12). The hardwood experiments 2 and 3 suggested that of the total charged oxygen 50-74 % (Run 2) and 55-80 % (Run 3) went into the oxidation of lignin and OWL, and into the formation of low-molecular-mass compounds. It was probable that in the case of Run 1 all the oxygen charged was used in the reactions since, according to the estimations, molecular oxygen consumption was 5-8 kg/BDt. The range in these figures was caused by the amount of oxygen the origin of which was not known for certain (either O_2 or HO^-). The amount of oxygen in the dissolved lignin was calculated according to the assumption that the lignin in the feed liquor had already been completely oxidized and had an oxygen content of 37.2 %.

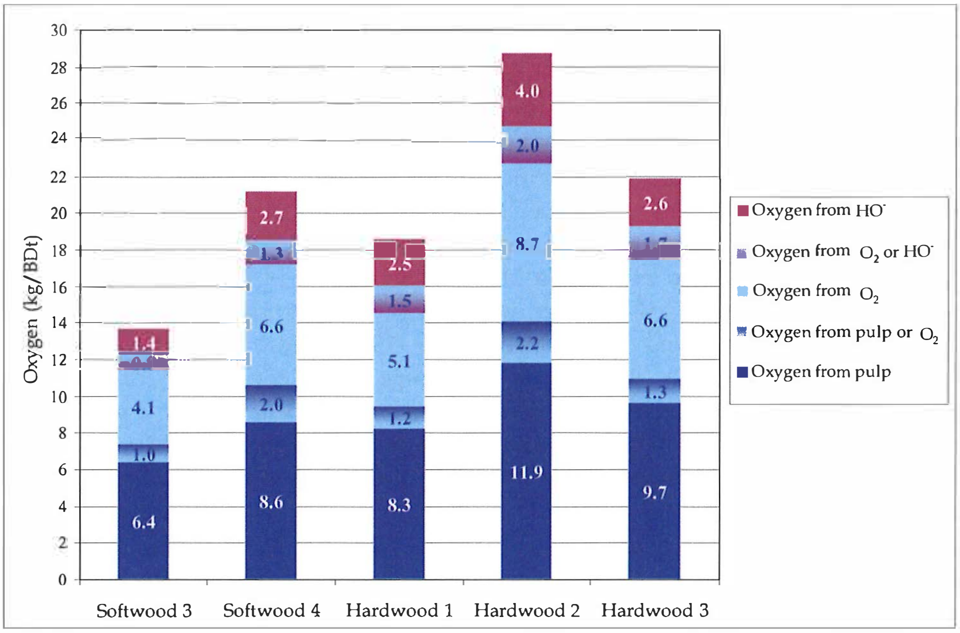


FIGURE 12 A rough estimation of the origin of oxygen in the dissolved reaction products of softwood and hardwood. Estimations take into account sulfur compounds in which case portion "oxygen from pulp" includes oxygen deriving from thiosulfate (amount in softwood cases 1.0 and 1.9 kg/BDt and in hardwood effluents 2.2, 4.0, and 3.0 kg/BDt).

4.2.2 General considerations

Some of the reaction products formed were not taken into account in the material balances and the amount of carbohydrates in pulp was calculated according to lignin content and yield loss calculations, which influence the accuracy of the estimations. For example, the amount of extractives in the pulp was not considered, although it probably was, at least to some extent, affected by oxygen delignification. There were also other minor reaction products, such as acetaldehyde, acetone, and carbon monoxide, which were not included in the balances. In spite of this, it could be concluded that, according to the relevant data in the literature, all the main reaction product components were accounted for. The reason for not performing the oxygen examination with bamboo was the lack of adequate information, for example, on the elemental composition of dissolved bamboo lignin.

The results of this study suggested a molecular oxygen consumption of 0.6-1.0 kg/BDt per unit of Δkappa for softwood and 1.0-2.0 kg/BDt per unit of Δkappa for hardwood pulp. If oxygen consumed by sulfur compounds is not taken into account, consumption of oxygen remains between 0.4 and 1.2 kg/BDt per unit of Δkappa. Reported oxygen consumption in industrial systems varies from 0.8 kg/BDt to 1.9 kg/BDt (McDonough, 1996; Berry *et al.*, 2002), the normal assumption being 1.4 kg/BDt for softwoods and 1.6 kg/BDt for hardwoods per decreased kappa number (McDonough, 1996). The hardwood results thus seem to accord with the general level whereas the softwood pulp estimations indicated a somewhat lower consumption than cited in the literature. In laboratory reactors oxygen consumption varies from 0.5 to 0.6 kg/BDt per unit kappa number reduction (Thompson and Corbett, 1976; Berry *et al.*, 2002). Oxygen consumption is expected to be higher in a commercial system than in laboratory reactors because of losses due to reactor venting and entrainment with the pulp leaving the reactor (Berry *et al.*, 2002).

Mill tests conducted by Hornsey *et al.* (1991) demonstrated that all the added oxygen (charge 9-16 kg O_2/t pulp) was consumed during the delignification process, although generally oxygen is charged in excess. The results for the most part conflict those obtained in the present study, which indicated that considerable amounts of molecular oxygen remain after industrial oxygen-alkali delignification, *i.e.*, 37-80 % of the charged oxygen was used in the reactions. It could be assumed that during the first hardwood delignification all of the oxygen charge (5.5 kg/ADt) was consumed in the reactions. One reason for the more active oxygen behavior in the mill trials by Hornsey and co-workers (1991) could be the higher process temperature (110-115 °C). It has been noted (Berry *et al.*, 2002) that oxygen consumption increases with temperature and that temperature seems to have a more critical effect on delignification along with the alkali charge than do oxygen charge or pressure.

Laboratory experiments and computer modeling studies have revealed that oxygen charge influenced, for example, kappa number only through interaction with oxygen pressure and other variables; thus increasing the oxygen charge from 1.0 to 5.0 % on pulp decreased kappa number only slightly (~3 kappa units) (Berry *et al.*, 2002). This was consistent with the results reported here, although the oxygen charge was smaller (0.6-1.8 % on pulp) than the range used by Berry *et al.* (2002). The optimal oxygen charge relative to the degree of delignification has been determined to be about 1.8 % w/w on o.d. pulp (Hart *et al.*, 2006). Generally the oxygen charge applied in commercial systems varies from 0.7 to 2.5 % (mean 1.6 ± 0.5 %) on pulp (Bennington and Pineault, 1999).

4.3 Yield and selectivity

4.3.1 Softwood and hardwood delignification

The results indicated a similar pulp yield of 97-98 % for both the softwood and hardwood oxygen delignification processes (Tables 16-17); however reaction selectivity appeared to be much lower for hardwood (~60 %) than softwood (70-80 %). The yield estimations were rather consistent with the yield values cited in the literature (Malinen, 1975; Pfister and Sjöström, 1979; Alén and Sjöström, 1991; Lai *et al.*, 1994; McDonough *et al.*, 1999), which vary in the range 94-98 % depending on wood species and the process conditions applied. For a specific degree of delignification, the differences in yield usually derive from differences in hemicellulose retention (Minor, 1996).

TABLE 16 Estimated yield loss, yield, and selectivity for softwood (I; II; III)

Method	Unit	Run 1	Run 2	Run 3[1]	Run 4
Yield loss I	kg/BDt	18.5	13.0	18.5	23.4
Yield loss II		21.2	14.8	15.1	25.7
Yield loss III		25.6	15.3	18.7	23.5
Yield I	%	98.2	98.7	98.2	97.7
Yield II		97.9	98.5	98.5	97.4
Yield III		97.4	98.5	98.1	97.6
Selectivity 1	%	87.2	90.3	83.1	72.7
Selectivity 2		60.9	73.7	56.4	66.9
Selectivity 3		76.5	77.7	81.1	74.3
Selectivity 4		79.5	83.3	81.5	80.2
Selectivity 5		87.3	90.0	86.2	82.3

[1] Deviation in yield loss in Run 3 was presumably caused by inaccuracy of the TOC analysis.

TABLE 17 Estimated yield loss, yield, and selectivity for hardwood (IV)

Method	Unit	Run 1	Run 2	Run 3
Yield loss I	kg/BDt	17.1	29.1	28.7
Yield loss II		18.4	21.4	21.4
Yield loss III		18.6	24.1	21.6
Yield I	%	98.3	97.1	97.1
Yield II		98.2	97.9	97.9
Yield III		98.1	97.6	97.8
Selectivity 1	%	59.0	58.6	54.6
Selectivity 2		49.0	44.8	46.2
Selectivity 3		60.2	58.6	69.2
Selectivity 4		61.2	56.9	68.6
Selectivity 5		58.9	63.0	67.0

The relatively high selectivity value for softwood delignification (~80 %) could be explained by the fact that in the processes studied, delignification was not continued to a level where different harmful carbohydrate degradation reactions would be pronounced. These values are similar to the ones obtained from literature (79-91 %) according to the relationship between viscosity and kappa number (Pekkala, 1984; Li *et al.* 1996; Allison *et al.*, 2000; Tamminen, 2005). The selectivity factor defined as the ratio of the rate constants for a selected pair of lignin and carbohydrate models reported by Ek *et al.* (1989) was between 5 and 6. Interestingly, when assuming equal amounts of possible reaction sites for lignin and carbohydrates in pulp, a reaction product ratio of 5-6 to 1, *i.e.*, a selectivity of 85 % is obtained.

The comparatively low selectivity of oxygen-alkali delignification of hardwood kraft pulp was interesting because it is typically considered to be a "mild" process with a lower degree of delignification than that applied to softwood kraft pulp. Although some of the conditions used were rather severe, low selectivity was also obtained for the relatively "normal" hardwood process (Run 1). However, Chen and Lucia (2003) have also noted a lower selectivity for hardwood compared to softwood under the same delignification conditions. In a study by Jansson *et al.* (1990), viscosity and kappa number reduction during oxygen delignification indicated a selectivity of 56-78 % for hardwood pulp. The reason for the greater carbohydrate loss of birch pulp may be a consequence of the high hemicellulose (xylan) content.

As discussed earlier (in chapters 2.3.1 and 4.1.1), the cause for lower selectivity of hardwood may be due to the linkages between residual lignin and hemicelluloses; especially owing to the different relative reactivity of lignin-xylan and lignin-glucomannan complexes. Other factors affecting selectivity could be unoxidised black liquor solids, which can be particularly detrimental to the effectiveness of oxygen delignification (Allison *et al.*, 2000). For example, dissolved lignin can consume alkali, lower pH, and slow fiber delignification. It can also lower process selectivity as it forms cellulose-degrading radicals without contributing to fiber delignification. Formic acid and xylose in the liquor have also been observed to affect the delignification response: formic acid has been shown to lower kappa number and raise brightness, and xylose to have the opposite effects (Sankari *et al.*, 2004).

There was, as expected, a difference in the delignification responses between the test runs. A lower yield and lower selectivity was estimated for runs with higher alkali and oxygen charge when comparing trial-pairs resulting in similar degree of delignification. A lower pulp yield in softwood Run 1 than in Run 2 was expected due to the difference in the degree of delignification (Δkappa 10.2 *vs.* 7.5). The difference between trials 3 and 4 could be attributed to the different amounts of oxygen used, since the process conditions were otherwise basically unchanged. These indications could, however, be considered only tentative because of the relatively small number of samples and possible minor differences in the feedstock pulps due to the different dates of sampling.

Selectivity has been found to increase when the oxygen charge was increased from 1 % to 2.5 %, but to decrease when the charge was further increased to 5 % (Berry *et al.*, 2002). In relation to this, an interesting question is whether the increased charge of molecular oxygen would have an effect on reaction selectivity. This question was studied in hardwood Runs 2 and 3 by trying to maintain the degree of delignification (Δkappa) and other process conditions the same while changing the oxygen charge. However, the OWL air oxidation process resulted in a different concentration of Na_2S in the different runs (11.3 g/l in Run 2 and 4.4 g/l in Run 3), which was not known at the time of the sampling. As a result of this, the oxidation of Na_2S to Na_2SO_4 in the liquor consumed a considerable amount of oxygen during the delignification process. The poor quality of the OWL is probably also the reason why no clear distinction in selectivity between different process conditions was observed. In addition to the quality of the OWL, the amount charged also raised some doubts about whether the amount displayed by the process control system was the actual amount charged in the process. In Run 3, particularly, the amount of OWL was exceptionally high. However, the pH values measured from the liquor samples (Table 12) indicated that more alkali was used in Run 3 than in Run 2 despite uncertainty as to the actual amount of OWL.

4.3.2 Bamboo delignification

The methods applied to the bamboo pulps resulted in estimated yields of 95-98 % for the oxygen delignification process (Table 18). The closest yield values to those determined gravimetrically (Table 14) were obtained by the Yield III method. The selectivity values for O_2-1 and O_2-2 were in the range 44-68 % and 52-67 %, respectively. These values were similar to those found for industrial birch kraft pulp most likely because of the similarities in hemicellulose content. Owing to the higher amount of residual lignin in kraft pulp 1, compared to that in kraft pulp 2, the yield loss was also slightly higher in the former case.

TABLE 18 Estimated yields and selectivities (%) of the oxygen delignification of bamboo

Method		O_2 - 1	O_2 - 2
Yield loss I	kg/BDt	36.0	27.9
Yield loss II		51.4	33.0
Yield loss III		28.2	21.3
Yield I	%	96.4	97.2
Yield II		94.9	96.7
Yield III		97.2	97.9
Selectivity 1	%	43.5	53.4
Selectivity 2		49.8	51.8
Selectivity 3		60.4	53.7
Selectivity 4		54.5	58.5
Selectivity 5		68.4	66.9

4.3.3 General considerations

With respect to the three yield estimation methods shown above, further discussion of their theoretical assumptions and limitations is merited. Yield I, measured from the dissolved solids material balance, ignored reaction water (*e.g.*, from neutralization) and easily volatile compounds, such as methanol. This fact probably had an effect on the results, which thus to some extent underestimated the yield losses and overestimated the corresponding yields.

Yield II assumed a certain relation between the material groups dissolved from the pulp fiber during the oxygen delignification treatment. The relationship of 1:1 between lignin and carbohydrates, as used in the calculations, may not be a general and accurate value for all cases. However, according to the existing literature, the assumption should be reasonable, and thus also lead to realistic values for yields. It is also thought to be more representative for general cases with prolonged delignification. In the case of assuming a 80/20 material loss for lignin/carbohydrates (as was the result in the softwood experiments) in the calculations, the corresponding Yield II would increase by 0.1-0.3 %.

Yield III was based on the analysis of the main individual components in the process liquors. However, it is likely that not all the reaction products formed were taken into account, as discussed earlier, although it was concluded that all the main reaction product components were taken into account. These main components (lignin, carbohydrates, methanol, formic and acetic acid, and hydroxy acids) accounted for 86-100 % of the total TOC measured for the liquors. Because of the increased amount of oxygen bound to the reaction products in comparison with the original material in the kraft pulp fibers, Yield III might still have a tendency to overestimate yield losses and thus underestimate the pulp yield.

For process control purposes, Yield I would be the most practical way of measuring yield. It is relatively fast and simple to perform. Yield II is also easy to measure if TOC analyzer is available but it requires a bit more effort if the liquor needs to be diluted before measurement. The above mentioned easiness of the methods applies only if the chemical charges do not have to be accounted for, *i.e.*, sampling sites are positioned in the way that the weight of alkali is included in the material balances. Yield III on the other hand is demanding and time consuming owing to the numerous different analyses needed and therefore is not suitable for process control, but it gives the most accurate description of the liquor composition. It also probably gives the most correct value for yield at least on the basis of the bamboo yield results if they are compared to their gravimetrical yields.

Also, some of the theoretical assumptions regarding the selectivity estimation methods used should be further discussed. Selectivity 1, measured by the dissolved carbon material balance, assumed a carbon content of 63-64 % in kraft lignin and a straight relationship between the "modified kappa number" and pulp lignin content. In practice these assumptions may not be very accurate, thus leading to some uncertainty in the results. There are, of course, more accurate ways of determining the lignin content of pulp but since kappa measurement is widely used in the industry the kappa-lignin-relationship simplifies the estimation. Nonetheless, according to the oxygen balances, the estimated amounts of material dissolved from pulp, although based on the above mentioned assumptions, correspond reasonably well to the products found in the liquor.

Selectivities 2 and 3 were based on the analysis of the main individual components present in the process liquors. These methods could be affected by the fact that not all of the reaction products formed were taken into account. Selectivities 2 and 3 might tend to overestimate the total amount of reaction products (Sum 1) and thus underestimate the selectivity, owing to the increased amount of oxygen bound to the reaction products compared with that bound to the original material in pulp. If selectivity 2 is calculated by deducting the assumed oxygen addition from the dissolved compounds, results indicate 1-5 % better selectivity. In addition, Selectivity 3 was based on a set of simple assumptions about the origin of each reaction product. Such an approach can only give a rough estimation for selectivity in oxygen delignification. The results for Selectivity 3 were highly comparable to those of the other methods.

Selectivity 4 was based on the formation of specific carbohydrate-derived reaction products during oxygen delignification. Clearly, not all such products were taken into account. However, if the value for K is close to 1, the values for Selectivity 4 would be close to the values obtained from Selectivities 1, 2, and 3.

The traditional way of expressing selectivity does not directly give the ratio of lignin-based reactions to carbohydrate reactions, or the amounts of lignin-derived reaction products to carbohydrate-derived products. Viscosity is an indirect measurement for the mean length of carbohydrate chains in pulp. Although there is no general and unambiguous relationship between selectivity and change in viscosity in pulps, a statistical relationship probably exists. One should pay attention to the significant distortion to the kappa measurement caused by HexAs when using this ratio. The viscosity to kappa number relation gives values such as 10 to 15, for example, for softwood (Steffes *et al.,* 1998). In order to reach the average level for selectivity, *i.e.,* 80 %, constant K would need a value of 1-2.

From the practical point of view only Selectivity 1 might be used in the industry for process control purposes in addition to the traditional way (Selectivity 5). The other methods need specific laborious analyses of the liquor components. That which is the best or most accurate way of determining the selectivity of oxygen delignification is difficult to determine, since there is not a good unambiguous way to measure selectivity for which to compare it to. All of the described methods are based on some kind of estimations and include assumptions to a certain degree.

A detailed comparison between the process concepts would have required clearly higher number of samples to obtain a statistically sound result, but the purpose of this study was not to validate a statistically acceptable way of measuring yield or selectivity but to test whether these methods give realistic values or have the potential to be used as a tool for comparing both varying pulp yields and selectivities obtained under different process conditions. Naturally, mill conditions and variability in delignification process causes error to the results which could be avoided in laboratory conditions. However, the methods of estimation presented here did show potential in describing the kraft pulp yield and selectivity of an industrial oxygen delignification process. Especially yield estimation methods might be useful since they gave results comparable to literature values and two of them are practical to utilize. On-line methods of analysis may be of use when implementing some of these estimation methods. For example, on-line kappa number measurement is widely used and UV absorption measurement of the pulping liquor (at 280 nm) is applicable as an indicator of the lignin content. The concentrations of dissolved solids, on the other hand, can be indicated by differential refractive index measurement (Paulonis and Krishnagopalan, 1991; Vanchinathan and Krishnagopalan, 1995). Also, a method for the rapid quantification of the acids commonly found in pulping liquors is under development (Käkölä and Alén, 2006).

5 CONCLUSIONS

The results showed that it is possible to describe the performance chemistry of an industrial oxygen delignification process by analyzing the dissolved material in detail and by using component material balances. The material balances confirmed that dissolved lignin, hydroxy acids, and carbonate are the main reaction products in a kraft pulp oxygen-alkali delignification process. In spite of the somewhat different chemical composition of bamboo pulps, compared to wood kraft pulps, the oxygen delignification bamboo kraft pulp resulted, for example, in the formation of the same carbohydrate-derived degradation products (*e.g.,* aliphatic carboxylic acids) as obtained during the oxygen delignification of birch kraft pulp.

The amount of charged molecular oxygen and OWL quality clearly impacted on the formation of the different groups of reaction products. It was observed that birch kraft pulps were more prone to degradation, which was seen in greater amounts of dissolved hydroxy monocarboxylic acids and volatile acids compared to that of softwood pulps. The more drastic oxidative depolymerization of xylan compared to cellulose or glucomannan is possibly due to physical factors such as solubility and accessibility. Structural differences between hardwood and softwood lignin as well as the nature of the residual lignin and LCCs in kraft pulp could also affect the relative reactivity of hardwood and softwood components towards bleaching chemicals.

Estimations on the origin of oxygen based on the dissolved reaction products revealed that 39-80 % of the charged oxygen was consumed during the oxygen delignification stage. The results thus suggested a molecular oxygen consumption of 0.6-1.0 kg/BDt per unit of kappa number reduction for softwood and 1.0-2.0 kg/BDt per Δkappa unit for hardwood kraft pulps. Oxidation of OWL components (Na_2S, $Na_2S_2O_3$, and Na_2SO_3) consumed a considerable portion of the molecular oxygen, especially in cases where the sulfide concentration in the liquor was high. The effect of oxygen charge on selectivity was difficult to determine on the basis of these trials.

The presented estimation methods based on component material balances gave realistic values for the kraft pulp yield and selectivity of an industrial oxygen delignification process as well as of the laboratory delignification of bamboo kraft pulp. The material balances corresponded to a pulp yield of

97-98 % for industrial wood pulps and 95-98 % for laboratory bamboo pulps. It was estimated that ~60 % of the hardwood and roughly 70-80 % of the softwood pulp material dissolved derived from lignin. Bamboo pulps had a selectivity similar to that of the birch pulps. A more detailed comparison between the process concepts would have required clearly higher number of samples to obtain a statistically sound result. Mill conditions and variability in delignification process causes some error to the results which could be avoided in laboratory conditions. However, the initial aim of this study was to find a way to describe the industrial process which would take account the variables absent in laboratory experiments. The methods of estimation presented here did show potential as a new and useful tool for comparing both varying pulp yields and selectivities obtained under different delignification process conditions. Especially the yield estimation methods might be useful since they gave results comparable to literature values and are relatively straightforward to utilize.

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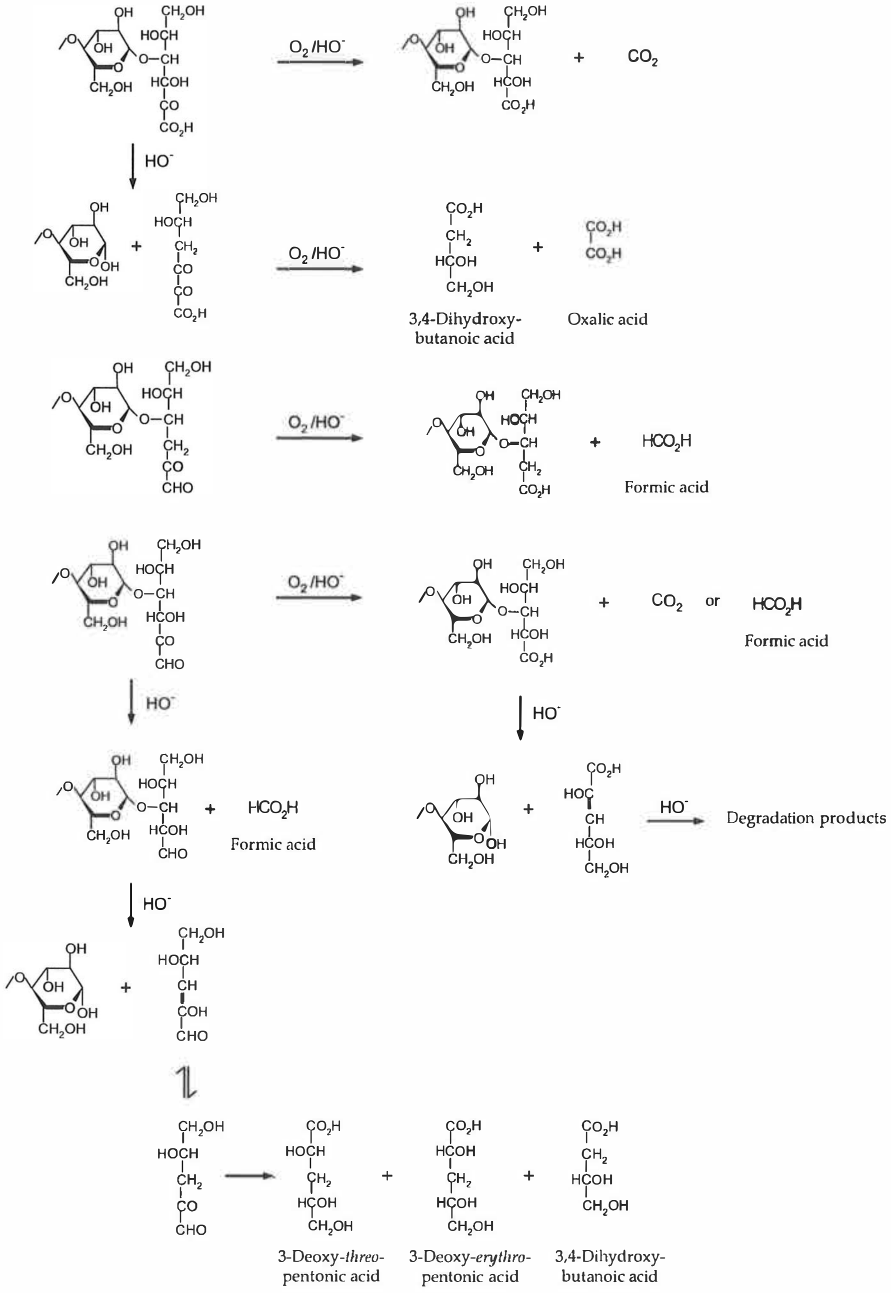
APPENDIX 1a

EXAMPLES OF PROPOSED REACTION PATHS FOR THE FORMATION OF THE MAIN REACTION PRODUCTS DURING OXYGEN DELIGNIFICATION

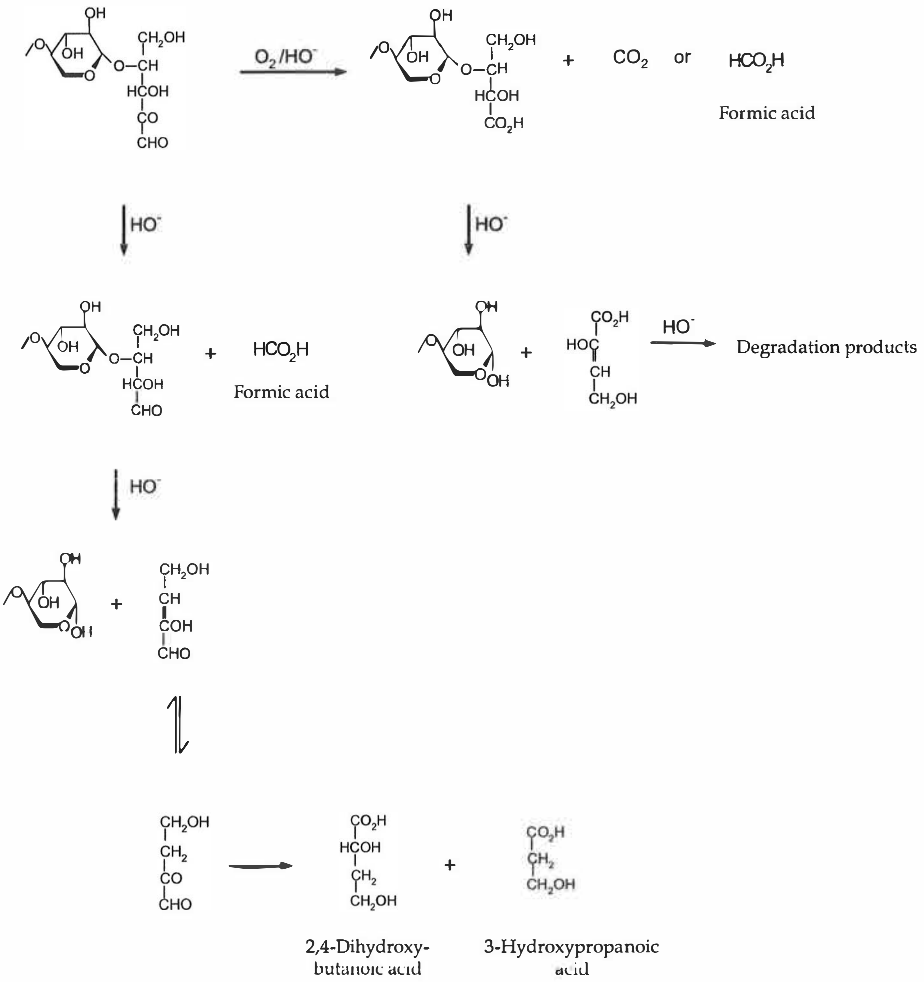
Degradation routes of intermediate end groups in alkaline oxidation of cellulose (Kolmodin and Samuelson, 1972; Ericsson *et al.*, 1973; Löwendahl and Samuelson, 1974; Malinen, 1974, 1975)



APPENDIX 1b

EXAMPLES OF PROPOSED REACTION PATHS FOR THE FORMATION OF THE MAIN REACTION PRODUCTS DURING OXYGEN DELIGNIFICATION

Degradation routes of intermediate end groups in alkaline oxidation of xylan (Malinen, 1974, 1975)



APPENDIX 2

OXYGEN CONTENT OF PULP AND LIQUOR COMPONENTS (%)

Component	Softwood		Hardwood	
	Kraft	O_2	Kraft	O_2
Pulp				
Carbohydrates[1,2]	48.9	48.9	48.8	48.8
Lignin	27.9[3]	29.8[3,4]	28.0[5,6]	29.0[6]
Liquor				
Carbohydrates[1,2]	48.9	48.9	48.8	48.8
Lignin	28.0[7]/37.2[4,7]	37.2[4,7]	28.0[5]/37.2	37.2
Methanol	49.9			
CO_3^{2-}	72.7			
$S_2O_3^{2-}$	42.8			
SO_3^{2-}	60.0			
SO_4^{2-}	66.6			
Acids				
Formic	69.5			
Acetic	53.3			
Glycolic	63.1			
Lactic	53.3			
3-Hydroxypropanoic	53.3			
Glyceric	60.3			
2-Hydroxybutanoic	53.3			
2,4-Dihydroxybutanoic	53.3			
3,4-Dihydroxybutanoic	53.3			
3,4-Dideoxypentonic	47.7			
3-Deoxy-*erythro*-pentonic	53.3			
3-Deoxy-*threo*-pentonic	53.3			
Xyloisosaccharinic	53.3			
α-Glucoisosaccharinic	53.3			
β-Glucoisosaccharinic	53.3			
Oxalic	71.1			
Tartronic	66.6			
Succinic	54.2			
Malic	59.7			

1 (Alén, 2000b)

2 (Gullichsen, 2000)

3 (Jiang and Argyropoulos, 1999)

4 (Sun and Argyropoulos, 1995)

5 (Gellerstedt *et al.*, 1988)

6 (Gellerstedt *et al.*, 1994)

7 (Gellerstedt and Lindfors, 1987)

APPENDIX 3

FORMULAS FOR THE ESTIMATIONS OF ORIGIN OF OXYGEN IN PULP AND LIQUOR COMPONENTS

Molecular oxygen needed for the oxidation of pulp lignin (kg/BDt):

O_{PO} (kg/BDt) - [O_{PK} (%)/100 * L (kg/BDt)]

L = OL (kg/BDt) * (1 - O_{PO} (%)/100) / (1- O_{PK} (%)/100)

Molecular oxygen needed for the oxidation of dissolved lignin (kg/BDt):

n(O)*M(O) = n(lignin)*M(O) = ΔLignin (kg/BDt) /185 (g/mol) * 32 (g/mol)

Molecular oxygen needed in the formation of volatile acids and oxygen originating from pulp components (kg/BDt):

½ O_{VA}

Oxygen in hydroxy acids originating from pulp components (kg/BDt):

O_{HA} - ΣO_{HA+}

O_{HA+} = M(O)/M(acid) * ΔAcid (kg/BDt)

Oxygen in hydroxy acids originating from molecular oxygen or OH^- (kg/BDt):

ΣO_{HA1+}

O_{HA1+} = M(O)/M(acid) * ΔAcid (kg/BDt)

Oxygen in hydroxy acids originating from OH^- (kg/BDt):

ΣO_{HA2+}

O_{HA2+} = M(O)/M(acid) * ΔAcid (kg/BDt)

L = amount of original non-oxidized lignin in oxygen delignified pulp
OL = Oxygen delignified lignin
O_{PK} = Oxygen in pulp kraft lignin (% or kg/BDt)
O_{PO} = Oxygen in oxygen delignified pulp lignin (% or kg/BDt)
O_{VA} = Oxygen in formed volatile acids (kg/BDt)
O_{HA} = Oxygen in formed hydroxy acids (kg/BDt)
O_{HA+} = Portion of additional oxygen in each individual acid (kg/BDt)
O_{HA1+} = Portion of additional oxygen in specific acids including glycolic, 3-hydroxypropanoic, glyceric, 3,4-dihydroxybutanoic, and dicarboxylic acids (kg/BDt)
O_{HA2+} = Portion of additional oxygen in specific acids including lactic, 2,4-dihydroxybutanoic, xyloisosaccharinic, and glucoisosaccharinic acids (kg/BDt)

ESTIMATION OF THE ORIGIN OF OXYGEN IN THE MAIN REACTION PRODUCTS OF SOFTWOOD KRAFT PULP (kg/BDt)

Component	**Molecular oxygen**		**Oxygen from alkali**		**Oxygen from pulp**		**Sum**	
	Run 3	**Run 4**	**Run 3**	**Run 4**	**Run 3**	**Run 4**	**Run 3**	**Run 4**
Lignin, in pulp	0 - 0.4	0 - 0.3	0 - 0.4	0 - 0.3				
Carbohydrates, dissolved					0.4	0.9	0.4	0.9
Lignin, dissolved[1]	1.7	1.9			2.6	3.0	4.3	4.9
Volatile acids	0 - 0.5	0 - 0.8	0 - 0.5	0 - 0.8	0.5	0.8	1.0	1.6
Hydroxy acids	0 - 0.3	0 - 0.5	0.1 - 0.4	0.1 - 0.6	1.1	1.7	1.4	2.4
Methanol					0.8	0.3	0.8	0.3
Carbonate	1.0 - 2.0	2.0 - 4.0	1.0	2.0	0 - 1.0	0 - 2.0	3.0	6.0
Sulfur compounds[2]	1.4	2.6	0.3	0.6	1.0[3]	1.9[3]	2.7	5.1
Total	4.4 - 6.6	6.6 - 10.2	1.4 - 2.6	2.7 - 4.3	6.4 - 7.4	8.6 - 10.6	13.6	21.2

ESTIMATION OF THE ORIGIN OF OXYGEN IN THE MAIN REACTION PRODUCTS OF HARDWOOD KRAFT PULP (kg/BDt)

Component	**Molecular oxygen**			**Oxygen from alkali**			**Oxygen from pulp**			**Sum**		
	Run 1	**Run 2**	**Run 3**	**Run 1**	**Run 2**	**Run 3**	**Run 1**	**Run 2**	**Run 3**	**Run 1**	**Run 2**	**Run 3**
Lignin, in pulp	0.2	0.2	0.2									
Carbohydrates, dissolved							0.9	0.7	0.3	0.9	0.7	0.3
Lignin, dissolved[1]	0.9	1.1	1.3				1.7	2.1	2.6	2.6	3.2	3.9
Volatile acids	0.0-1.0	0-1.3	0-1.3	0-1.0	0-1.3	0-1.3	1.1	1.4	1.4	2.1	2.7	2.7
Hydroxy acids	0-0.6	0-0.9	0-0.4	0.1-0.7	0.2-1.1	0.2-0.6	1.8	2.9	1.9	2.5	4.0	2.5
Methanol							0.6	0.8	0.5	0.6	0.8	0.5
Carbonate	1.2-2.4	2.2-4.4	1.3-2.6	1.2	2.2	1.3	0-1.2	0-2.2	0-1.3	3.6	6.6	3.9
Sulfur compounds[2]	3.0	5.4	4.0	0.8	1.4	1.0	2.2[3]	4.0[3]	3.0[3]	6.0	10.8	8.0
Total	5.3-8.1	8.9-13.2	6.8-9.9	2.1-3.7	3.8-6.0	2.5-4.2	8.3-9.5	11.9-14.1	9.7-11.0	18.3	28.8	21.8

[1] Calculated on the assumption that dissolved lignin has an oxygen content of 37.7 % before oxygen delignification

[2] Calculated from the amount of SO_4^{2-} formed according to the net reaction scheme: $Na_2S_2O_3 + 2\ NaOH + 2\ O_2 \rightarrow 2\ Na_2SO_4 + H_2O$

[3] For sulfur compounds, oxygen from $Na_2S_2O_3$

ORIGINAL PAPERS

I

ESTIMATION OF PULP YIELD IN INDUSTRIAL OXYGEN-ALKALI DELIGNIFICATION OF SOFTWOOD KRAFT PULP

by

Kari Ala-Kaila, Maria Salmela & Raimo Alén 2002

Nordic Pulp and Paper Research Journal 17(4), 401-404

https://doi.org/10.3183/npprj-2002-17-04-p401-404

II

ESTIMATION OF SELECTIVITY IN INDUSTRIAL OXYGEN-ALKALI DELIGNIFICATION OF SOFTWOOD KRAFT PULP

by

Kari Ala-Kaila, Maria Salmela & Raimo Alén 2002

Nordic Pulp and Paper Research Journal 17(4), 405-409

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III

FATE OF OXYGEN IN INDUSTRIAL OXYGEN-ALKALI DELIGNIFICATION OF SOFTWOOD KRAFT PULP

by

Maria Salmela, Raimo Alén & Kari Ala-Kaila 2004

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IV

DESCRIPTION OF AN INDUSTRIAL OXYGEN-ALKALI DELIGNIFICATION PROCESS OF BIRCH KRAFT PULP USING DISSOLVED MATERIAL ANALYSIS

by

Maria Salmela, Kari Ala-Kaila & Raimo Alén 2006

Journal of Pulp and Paper Science 32(1), 14-18

https://www.researchgate.net/publication/287627969

V

OXYGEN-ALKALI DELIGNIFICATION OF BAMBOO KRAFT PULP

by

Maria Salmela, Raimo Alén & Mân Thi Hong Vu

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