Apparent and actual delignification response in industrial oxygen–alkali delignification of birch kraft pulp

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ABSTRACT: The time-dependent behavior of material that affects the kappa number of birch kraft pulp was experimentally tested in an industrial, two-stage, oxygen–alkali delignification process. The pulps were leached, and the leached material was divided into four different fractions: the wash loss fraction and the easily leachable, slowly leachable, and stagnant fractions. These fractions were further characterized according to their chemical natures, representing residual lignin, extractives, hexenuronic acids, and other chemical structures contributing to the kappa number of the pulps. The apparent and actual delignification responses in the two reactors and the effects of the leaching operation were thoroughly evaluated based on the behaviors of these different pulp components.

Application: Improved procedures for measuring and reporting the results of delignification could lead to better evaluation and control of a modern oxygen delignification process.

Traditionally determined through oxidation with an acidic permanganate solution, the lignin content of chemical pulp is expressed as the kappa number of the pulp. The change in the kappa number is commonly measured as the response of pulp to oxygen–alkali delignification, or oxygen delignification, a process in which oxygen and alkali remove much of the residual lignin in unbleached kraft pulp [1–4]. However, the kappa number is somewhat ambiguously related to the lignin content in chemical pulps [5]. On the other hand, the amount of lignin, which may be located differently in the fiber [6–8], should be considered a transient parameter. It is transient, or time-dependent, because the kappa number of the pulp depends to a considerable extent on the success of washing and/or leaching [9–16].

To better understand the delignification response, Ala-Kaila and Reilama conducted leaching experiments with softwood kraft pulp in conjunction with kappa number determinations [17]. They divided residual material affecting the kappa number into four different fractions, representing wash loss and the easily leachable, slowly leachable, and stagnant fractions in pulps. They also discussed extensively the complexities of the delignification response.

Recently, Li and Gellerstedt reported on the structural significance of kappa number measurement [18]. They observed that components other than residual lignin contribute to the kappa number of chemical pulps—extractives, hexenuronic acids (HexA), and some other chemical structures with double bonds and/or carbonyl groups. Thus, an ordinary kappa number includes all the oxidizable chemical components that affect permanganate consumption [19]. Therefore, a more accurate way of estimating the actual residual lignin content may be more useful than determining the kappa number. One such measurement is the Oxymercuration-Demercuration (Ox-Dem) kappa number, which reflects only the contribution from residual lignin [20, 21]. On the other hand, it would also be useful to take into account the fundamental time-dependent behavior of residual components in chemical pulps to get a broader perspective on the overall efficiency of the process. To date, most work on the transient behavior of residual pulp components has been done with softwood pulps, and information is limited on the transient behavior of residual components in hardwood kraft pulps [8, 14,15].

Consequently, we experimentally tested the delignification response for birch kraft pulp in an industrial, two-stage oxygen delignification process. In this study, all chemical components contributing to the kappa number of the pulp are referred to as "apparent" lignin in contrast to "actual" lignin, or residual lignin (*i.e.*, polymeric material, consisting of phenylpropane units). The lignin removed, or the apparent lignin, represents not only the residual lignin but also extractives, HexA, and other chemical structures that contribute to the kappa number of the pulp. To put it another way, the ordinary delignification determination is referred to as the "apparent" response, and the Ox-Dem kappa number determination is referred to as the "actual" delignification response.

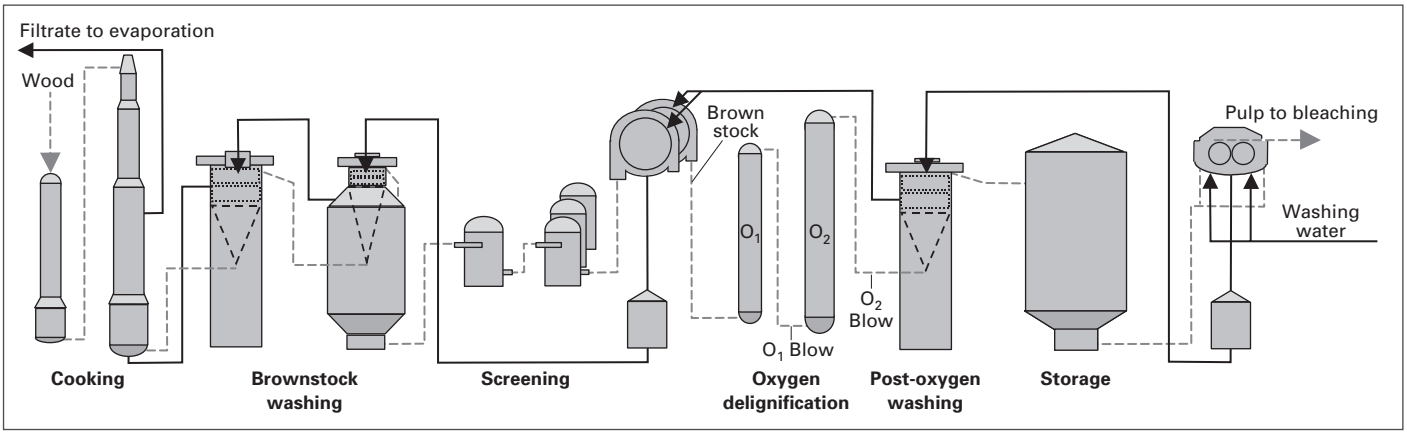
EXPERIMENTAL

Pulp samples

Samples of Scandinavian birch kraft pulp were taken at different steps along a two-stage oxygen delignification process. The total mill process consisted of a continuous digester followed by two brownstock diffusion washers, a screen room decker, and two medium-consistency oxygen delignification reactors with a double diffuser in post-oxygen washing. The mill's configuration is shown in **Fig. 1**. The actual sampling positions were: (a) pulp discharged from the brownstock decker, (b) pulp from the first reactor ("O_1 blow"), and (c) pulp from the second reactor blow tank ("O_2 blow").

The production rate was 1700 admt/day. In the first reactor, pulp at 10% consistency was retained for 15 min at 92°C with chemical charges of 4 kg NaOH/admt, 16.5 kg of oxidized white liquor/admt, and 10.5 kg O_2/admt. In the second reactor, pulp at 10% consistency was retained for 65 min at 96°C with a chemical charge of 2 kg O_2/admt.

The sampling procedure involved collecting two 10 L individual samples from each position at intervals corresponding



1. Process configuration.

	BROWNSTOCK		O_1 BLOW		O_2 BLOW	
Fraction	**Apparent**	**Actual**	**Apparent**	**Actual**	**Apparent**	**Actual**
Wash loss	5.4	…	5.5	…	5.5	…
Easily leachable	0.8	0.3	0.2	0	0.3	0
Slowly leachable	2.0	1.4	0.9	0.7	0.6	0.3
Stagnant	13.9	6.5	11.6	4.7	10.4	3.7
Total kappa no.	22.1	8.2	18.2	5.4	16.8	4.0

Wash loss = initial kappa no. (centrifuged pulp) – kappa no. after 2 min washing.
Easily leachable = kappa no. after 2 min washing – kappa no. after 30 min leaching.
Slowly leachable = kappa no. after 30 min leaching – kappa no. after 24 h leaching.
Stagnant = kappa no. after 24 h leaching.

I. Approximated fractions of apparent and actual residual lignin in kappa number units.

	BROWNSTOCK			O_1 BLOW			O_2 BLOW		
	2 min	**30 min**	**24 h**	**2 min**	**30 min**	**24 h**	**2 min**	**30 min**	**24 h**
Pulp kappa no.	16.7	15.9	13.9	12.7	12.5	11.6	11.3	11.0	10.4
Residual lignin[1]	8.2	7.9	6.5	5.3	5.4	4.7	4.1	4.0	3.7
Extractives[2]	1.5	1.2	1.0	1.2	0.9	1.0	1.0	0.9	0.8
HexA[3]	6.8	6.2	5.8	5.8	5.3	4.7	5.8	5.1	4.6
Others[4]	0.2	0.6	0.6	0.4	0.9	1.2	0.4	1.0	1.3

[1]Ox-Dem kappa number. [2]Kappa number reduction caused by acetone extraction. [3]0.086 × the content of HexA in pulp, mmol/kg [22]. [4]Kappa number after acetone extraction – kappa number from HexA – Ox-Dem kappa number.

II. Partial kappa numbers of pulp components after leaching at intervals of 2 min, 30 min, and 24 h.

to the retention times between the sampling points. The two samples from each position were mixed together and homogenized within half an hour of the initial mill sampling. The homogenized pulp samples were centrifuged to approximately 35% consistency.

Leaching experiments and analytical determinations

Leaching experiments were carried out within two hours of the initial mill sampling and were conducted with three identical leaching tanks. Each leaching tank was a round, covered plastic tank (14 L, diameter = 300 mm) placed in a water bath at 90°C. Each tank, filled with deionized water (9 L), was equipped with a manual sampling system and a laboratory mixer set at 150–200 rpm. The surface of the pulp was flushed with nitrogen gas throughout the experiments to prevent air oxidation during leaching. Similar leaching equipment has also been used in some earlier studies [14, 17, 22].

Centrifuged pulp (800 g wet) was placed in the leaching tank to form a fiber suspension of approximately 3% consistency. In all, three 2 L pulp samples were taken from the leaching tank at time intervals of 2 min., 30 min., and 24 h after the pulp was added. Each of these suspensions was centrifuged immediately after sampling, and some of the centrifuged pulp (200 g wet) and filtrate (500 mL) was collected for further analysis. The rest of the pulp and filtrate was placed back in the leaching tank. The pulp samples before leaching, after 2 min, after 30 min, and after 24 h of leaching were characterized in terms of kappa number [19], kappa number after acetone extraction [23], kappa number from HexA (calculated from the content and the oxidation equivalent of HexA) [23], and Ox-Dem kappa number [20].

RESULTS

By performing leaching experiments at different time intervals, we removed some dissolved material from the pulps. The residual pulp components could then be approximated into four different fractions. The first fraction was defined as the wash loss fraction, which could be removed from the pulps with a two minute washing. (The two minute leachate is coupled with the term "washing" because the time is considered to be too short for actual leaching to occur.) The fraction removed by 30 min of leaching was defined as the easily leachable fraction. The third fraction, defined as the slowly leachable fraction, was removed in the last part of the leaching experiment (24 h). The kappa-influencing components remaining in the pulp after the leaching experiments were defined as the stagnant fraction.

	BROWNSTOCK			O_1 BLOW			O_2 BLOW		
	Easily leachable	Slowly leachable	Stagnant	Easily leachable	Slowly leachable	Stagnant	Easily leachable	Slowly leachable	Stagnant
Residual lignin	0.3	1.4	6.5	–0.1[1]	0.7	4.7	0.1	0.3	3.7
Extractives	0.3	0.2	1.0	0.3	–0.1[1]	1.0	0.1	0.1	0.8
HexA	0.6	0.4	5.8	0.5	0.6	4.7	0.7	0.5	4.6
Other	–0.4[2]	0	0.6	–0.5[2]	–0.3[2]	1.2	–0.6[2]	–0.3[2]	1.3
Total	0.8	2.0	13.9	0.2	0.9	11.6	0.3	0.6	10.4

[1]Caused by experimental error (±0.1 for kappa number determination).
[2]Indicates an increase in the amount of other components.

III. Chemical compositions of different fractions of apparent lignin in the pulps (expressed in kappa number units).

The amounts of each fraction could be expressed as apparent lignin using the differences between ordinary kappa numbers and as actual residual lignin using the differences between the Ox-Dem kappa numbers. All four fractions were expressed as partial kappa numbers. For each pulp sample, the sum of these four fractions was equal to the ordinary total kappa number before any leaching (**Table I**).

We further characterized the "pulp" kappa numbers, according to the chemical nature of the removed material by dividing various kappa numbers into specific parts. The pulp samples after 2 min, 30 min, and 24 h of leaching were treated in the laboratory to remove extractives and to determine the HexA content. Comparisons between different measured and calculated kappa numbers resulted in three new specific parts of the total kappa number other than the kappa number based on actual residual lignin. These three parts were the kappa numbers from extractives, from HexA, and from other components (**Table II**).

The chemical compositions of different fractions were deduced from the differences before and after each individual leaching operation (**Table III**). From Tables II and III, we deduced the effects of leaching and the effects of both stages of oxygen delignification on the removal of different pulp components (**Table IV** and **V**).

DISCUSSION

Effects of leaching on different pulp components

The leaching experiments showed that most of the leached apparent lignin was present in the wash loss fraction—*i.e.*, approximately 5 units of kappa number (Table I). This result was evident although the original pulp was centrifuged up to 35% consistency before any leaching experiments. Further kappa number reductions were detected each time during the actual leaching experiments. The easily and slowly leachable fractions corresponded to up to two kappa number units in the pulp. The amount of easily leachable apparent lignin was about one third of the amount of slowly leachable apparent lignin. Most of the apparent lignin in pulps appeared as a stagnant fraction—*i.e.*, apparent lignin with no detectable response during the 24 h leaching experiment.

	Residual lignin	Extractives	HexA	Other
Brownstock	1.7	0.5	1.0	–0.4*
O_1 blow	0.6	0.2	1.1	–0.8*
O_2 blow	0.4	0.2	1.2	–0.9*

*Implies an increase in the amount of other components.

IV. Effects of a 24 h leaching on the removal of different pulp components after a 2 min washing (in kappa number units).

Changes in the amounts of different pulp components during the 24 h leaching experiment are shown in Table IV. The leaching procedure had a particular impact on brownstock pulp, with clear effects on the residual lignin, extractives, and HexA. The removal of residual lignin was more pronounced for brownstock pulp (1.7 units) than for oxygen-delignified pulps (0.6/0.4 units). This outcome was probably brought about by the removal of part of the leachable lignin from the pulps during the oxygen stages. A similar case could be made for the observed loss of extractives, which is probably attributable to the alkaline conditions applied in the stages.

On the other hand, the removal of HexA in leaching was fairly constant (about 1 unit) for all the pulps measured (Table III). As previously observed [23], the process conditions applied to oxygen delignification may not be strong enough to chemically modify the structure of HexA. Thus the small changes in the HexA contents in pulps are most probably caused by the dissolution of the HexA-containing pulp xylan into alkaline solutions. Furthermore, HexA was more pronounced in easily leachable fractions than was lignin (Table III), whereas lignin was more pronounced in slowly leachable fractions. These observations may be related to the differences in the structure or the location of the various components in or on the fibers.

	1st Stage	2nd Stage
2 min washing		
Residual lignin[1]	2.9	1.2
Extractives	0.3	0.2
HexA	1.0	0
Others	–0.2[2]	0
24 h leaching		
Residual lignin[1]	1.8	1.0
Extractives	0	0.2
HexA	1.1	0.1
Others	–0.6[2]	–0.1[2]

[1]Reduction in Ox-Dem kappa number.
[2]Implies an increase in the amount of other components.

V. Removal of different pulp components in two-stage oxygen delignification (kappa no. units).

A leaching operation means an additional weak alkaline wash of residual lignin, HexA or xylan, extractives, and other components. Leaching might also cause additional chemical reactions of pulp components under these slightly alkaline conditions (residual alkali after an incomplete washing, pH 9–10) at a relatively high temperature (90°C). Comparing the results of the leaching operation at different time intervals, we found that the amounts of HexA decreased and the amounts of the other components fraction increased systematically (expressed as negative data). Surprisingly, the sums of HexA and the other components fraction were practically constant (about 6 kappa number units) in oxygen-delignified pulps (Table II). (The dissolution of monosaccharides, such as glucose and xylose, during a leaching operation has been reported earlier [10]. The formation of double

bonds or aromatic structures from carbohydrates under similar conditions has also been noted elsewhere [24].)

Delignification response in two-stage oxygen delignification

Residual apparent lignin in pulps at each position along the oxygen delignification process corresponded to almost equal parts for residual lignin (Ox-Dem kappa number) and HexA (kappa number from HexA) (Table II). In addition, minor roles in partial kappa numbers were detected for extractives and for other components. All these four main components were present in all the pulps measured.

The results in Table II for kappa number after washing for 2 min show a reduction of 4.0 units (16.7 – 12.7) in the first reactor and 1.4 units (12.7 – 11.3) in the second reactor .These results reflect the apparent delignification response, or the apparent reduction of lignin content in the pulps. However, the actual delignification response was 2.9 kappa number units in the first reactor and 1.2 units in the second reactor (Table V). In the first reactor, the kappa number was reduced by 1.0 units with the removal of HexA and by 0.3 units (1.5 – 1.2) with the removal of extractives. We also noticed a small increase of 0.2 units (1.2 – 1.0) in the fraction of other components. For the second reactor, we observed a decrease of 0.2 units with the removal of extractives but no change in HexA or in the fraction of other components.

As a result of leaching, slightly different conclusions may be drawn. The delignification response in both reactors consisted of a change in the leachable and stagnant fractions of apparent lignin. Noticeable reductions of the easily and slowly leachable fractions were observed for the first reactor. The total delignification response in the second reactor was smaller than in the first reactor. The second reactor had an effect on the slowly leachable fraction, and the second reactor further reduced the stagnant fraction of apparent lignin. The responses, measured from the stagnant fractions, were 2.3 units (13.9 – 11.6) in the first reactor and 1.2 units (11.6 – 10.4) in the second reactor (Table I). They were somewhat lower than the responses measured directly from the samples with two minute washing. To estimate actual delignification responses from the leached pulps, we assigned 1.8 and 1.0 units of delignification to the first and second reactors, respectively (Table V). The differences between the apparent and actual delignification were again evidently caused by the removal of various pulp components other than lignin.

Chemically, the removal of residual lignin is attributed to the oxidation of aromatic structures, resulting in a further dissolution of the fragmented lignin into the alkaline solution. The response of the lignin oxidation being lower in the second reactor than in the first is thought to be a "clearing off" of the available and/or active lignin structures by the first oxygen-alkali stage. Besides this oxidation, the alkaline solution applied may also simply dissolve out or decompose part of extractives and HexA. The HexA removed is probably located at the surface of the fibers, such that most of this removal (1 kappa number unit) takes place in the first reactor. A negative removal, or an increase, of the fraction of other components takes place in the first reactor. This result means that some oxidizable structures were formed, probably from carbohydrate structures, during the oxygen delignification process. This kind of behavior has also been observed earlier [25].

Birch kraft pulp compared with softwood

We made some interesting observations when we compared the results of birch kraft pulp with the results for softwood kraft pulp obtained earlier [17]. This comparison between the wood species provided only superficial comparisons because there were significant differences between the studies in the process details and conditions used. In general, however, the stagnant fraction of apparent lignin showed a much lower percentage decrease for birch kraft pulp than for softwood kraft pulp (25% for birch, 60% for softwood [17]).

Surprisingly, the amounts of wash loss apparent lignin were exactly the same at all measured points for softwood and birch kraft pulp. The total amount of leachable apparent lignin (easily and slowly leachable together) for the softwood was also similar to that found for the birch. The total amount of leachable apparent lignin was somewhat higher for brownstock birch (2.8 kappa number units) than for softwood kraft pulp (2.2 kappa number units). However, for both types of pulp, the apparent lignin leached out by about the same amount after each step of oxygen delignification (about 1 kappa number unit) [17].

CONCLUSIONS

The delignification response for birch kraft pulp consists of different changes in the various chemical components that affect the kappa number. These components are the residual lignin, extractives, HexA, and some other specific chemical structures. The degree of delignification, measured as a change in kappa number, was 50% from residual lignin (from 8.2 to 4.1 in Table II), with 15% from HexA and 33% from extractives. Thus, expressing the total degree of delignification as 32% (from 16.7 to 11.3) is not very informative.

The transient, or time-dependent, behavior of apparent lignin in pulp may have a significant effect on the delignification response measured in an industrial oxygen delignification process, depending on the washing treatment before the analysis. Unbleached birch kraft pulp contains a considerable amount of apparent lignin that is in a transient state and has not had the chance to leach out of the fibers before oxygen delignification. Consequently, there is a risk that unbleached pulp may be characterized on the basis of a pulp sample that still contains leachable apparent lignin that has been affected in cooking but has not yet had the right conditions or enough time to be removed from the pulp fibers.

The procedure for measuring kappa number may have a noticeable effect on the performance characteristics reported for an industrial oxygen delignification process. Part of the delignification response is attributable to the enhanced removal of leachable components in pulp fibers. The real effect of oxygen delignification would be rather moderate if the degree of delignification were estimated according to the stagnant fractions of apparent lignin.

Finally, the washing procedure before kappa number analysis is vital in determining the amount of actual delignification attributable to either cooking or

oxygen delignification. The results also underline the importance of thorough washing in the mill in order to realize the full environmental benefits of an oxygen delignification process. **TJ**

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INSIGHTS FROM THE AUTHORS

The study was performed in order to build a wider and more proper picture of the delignification response taking place in industrial oxygen-alkali delignification of kraft pulp. The study complements and deepens our earlier studies on the step-wise delignification response in industrial oxygen-alkali delignification processes, and provides new ways to compare hardwood and softwood responses. We focused particularly on the chemical and dynamic character of the response.

The most difficult step of the study was determining how to build a clear set of definitions for the different types of chemical and dynamic fractions involved, and how to maintain them throughout the manuscript.

This study offers a new perspective with which to evaluate and explain different apparent and actual observations in industrial oxygen-alkali delignification processes. The results help mills to accept differences in delignification response between different mill processes and between different wood species. Mill personnel are able to set more realistic goals for industrial oxygen-alkali delignification processes when they are aware of the apparent and actual behavior.

The next step will be to compare the delignification response of softwood kraft pulp, originating from the same industrial process, to hardwood kraft pulp, using exactly the same experimental and analytical procedures—this is how real differences between the wood species could be observed. We are also interested in studying how to estimate the pulp yield and reaction selectivity under real mill conditions. Both of these attempts are continuing.

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