ORIGINAL ARTICLE

Soo-Jeong Shin · Nam-Seok Cho · Yuan-Zong Lai

Residual extractives in aspen kraft pulps and their impact on kappa number and Klason lignin determination

Abstract We investigated the impact of residual extractives on lignin determination by lignin content difference between unextracted and extracted pulps, residual extractives analysis, and lignin content contribution from model extractive compounds. There were two different kinds of extractives in aspen kraft pulp. The extractives impacting on kappa number determination were well removed in oxygen delignification; these were mainly unsaturated fatty acids. However, the extractives impacting on Klason lignin determination were largely resistant to oxygen delignification; these were mainly saturated fatty acids, sterols, and hydrocarbons. Oxidation of unsaturated fatty acids was the main reaction in oxygen delignification. These trends were confirmed by simulation of lignin content determination with three model extractive compounds (β-sitosterol, linoleic acid, and palmitic acid).

Key words Extractives · Kraft pulps · Oxygen-delignified pulps · Kappa number · Klason lignin

Introduction

Although pitch problems mainly occur in acid sulfite and mechanical pulp mills, these problems also have occurred in kraft pulp mills when aspen or birch woods were used in winter seasons with difficulty in debarking.[1] Significant amounts of pitch deposition on the process equipment or in the finished pulp products can occur. Pitch is primarily composed of lipophilic extractives, consisting mainly of fatty acids, sterols, steryl esters, and waxes. The low ratio of saponifiables to unsaponifiables in hardwood is a contributing factor to the frequent pitch problems in hardwood kraft mills.[2]

We previously reported the residual extractives in pine and aspen kraft pulps.[3] There were significant amounts of residual extractives in aspen pulps, but not in pine pulps. These residual extractives in aspen pulps affect lignin determination in terms of both kappa number and Klason lignin. The extractives impacting on kappa number were well removed but those extractives impacting on Klason lignin were resistant in oxygen delignification. Therefore, we expected the existence of two different types of residual extractives in unbleached aspen kraft pulps; one is easily removed in oxygen delignification and affects kappa number and brightness, the other is resistant in oxygen delignification and affects Klason lignin determination. In this study, we investigated the impact of two different types of residual extractives in unbleached and oxygen-delignified kraft pulps on lignin determination based on kappa number and Klason lignin.

S.-J. Shin[1] · Y.-Z. Lai
Faculty of Paper Science and Engineering, State University of New York, College of Environmental Science and Forestry (SUNY-ESF), New York 13210, USA

N.-S. Cho (✉)
Wood and Paper Science, School of Forest Resources and Rural Engineering, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea
Tel. +82-43-261-2542; Fax +82-43-273-2241
e-mail: nscho@chungbuk.ac.kr

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Present address:
[1]Wood and Paper Science, School of Forest Resources and Rural Engineering, Chungbuk National University, Chungbuk 361-763, Korea

Materials and methods

Kraft pulping and oxygen delignification

Trembling aspen (*Populus tremuloides* M.) was selected for the study. Kraft pulping was carried out under the following conditions: liquor to wood ratio, 4:1; T_{max}, 170°C; time to T_{max}, 60 min; time at T_{max} adjusted depending on H-factor; 15% effective alkali as Na_2O basis; 30% sulfidity. Oxygen delignification was conducted in a Quantum Mark IV reactor at 10% consistency, 100°C, 0.7 MPa O_2 pressure, and 60 min with 2% NaOH and 0.5% $MgSO_4 \cdot 7H_2O$ based on oven-dried pulp.

Extraction of pulps and analysis

Air-dried kraft or oxygen-delignified pulps (10 g, oven-dried basis) were extracted as described in TAPPI test method T204 cm-97.[4] Ethanol–benzene (1:2, v/v, 250 ml) was used as the extracting solvent. Air-dried wood chips were milled in a Wiley mill to 40–60 mesh. An air-dried wood meal sample (5 g oven-dried basis) was similarly extracted as for kraft pulps.

After Soxhlet extraction, the solvent in the extraction flask was partially evaporated in a rotary evaporator under reduced pressure to a volume of 5 ml. This concentrated substance was kept in a refrigerator, and was used directly for gas chromatography-mass spectrometry (GC-MS) analysis without prior derivatization.[5]

Simulation of lignin content determination with model extractive compounds

For kappa number, extractive model compound was dissolved in 20 ml of p-dioxane and then diluted with 20 ml of distilled water. The permanganate oxidation was carried out as described in TAPPI test method 236 om-99.[6]

For Klason lignin, extractive model compound (0.40 g) was mixed with 1 g of cotton linter cellulose. The Klason lignin content was determined by TAPPI test method T222-om-98[7] and TAPPI useful method UM 250 was used for acid-soluble lignin.[8] The impact of extractives on lignin determination was evaluated by lignin content difference between unextracted and extracted pulps, and calculated by the following formula:

$$\% \text{ Contribution to lignin content} = \frac{L_u - L_e}{L_e} \times 100$$

where L_u is the lignin content of unextracted pulps and L_e is the lignin content of extracted pulps.

Results and discussion

Impact of extractives on lignin determination

Pulp yield, kappa number, and residual extractives in unbleached and oxygen-delignified kraft pulps are given in Table 1. We evaluated the impact of extractives on lignin determination by lignin content difference between unextracted and extracted pulps.

Table 1. Yields, kappa numbers, and residual extractives of unbleached kraft pulps prepared from aspen

H-factor	Pulp yield (%)	Kappa number	Residual extractives (%)
650	56.9	26.1	1.0
950	56.2	16.0	0.9
2300	54.9	9.5	0.5

As pulping progressed (increasing H-factor), extractives and lignin in wood chips were dissolved to black liquor, which resulted in lower residual extractives content in pulps cooked at higher H-factor condition. Main reactions of extractives in kraft pulping are alkaline hydrolysis of steryl esters or triglycerides, ionization of carboxylic acid to carboxylate, and dissolution of neutral extractives assisted by resin acid and fatty acid.[9]

Residual extractives in kraft pulps impacted on lignin determination by both kappa number and Klason lignin methods. In the case of aspen pulp, residual extractives contributed more to Klason lignin than kappa number (see Figs. 1 and 2).
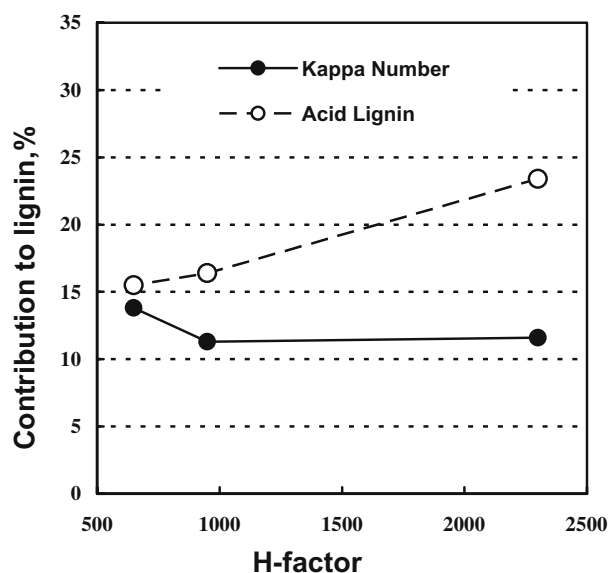

Fig. 1. Impact of extractives on lignin determination (unbleached kraft pulps)
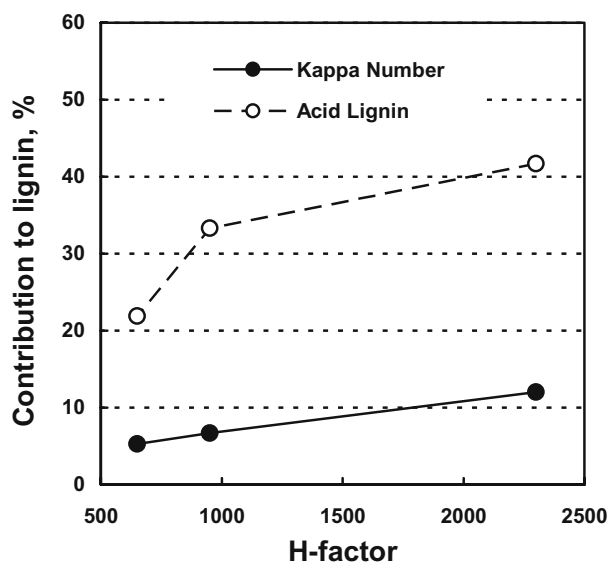

Fig. 2. Impact of extractives on lignin determination (oxygen-delignified kraft pulps)
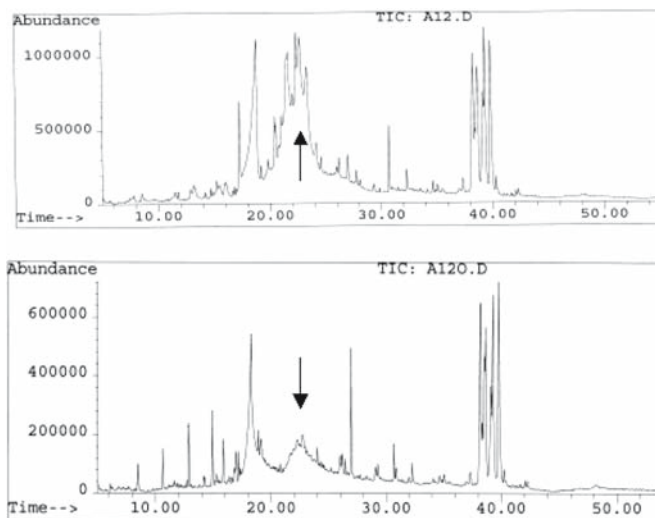
Fig. 3. Total ion chromatogram (*TIC*) of unbleached (*top*) and oxygen-delignified aspen kraft pulps (*bottom*) (H-factor 2300 pulps) showing decreased linoleic acid peak (*arrow*) in oxygen delignification

Table 2. Residual extractives from aspen unbleached kraft pulp identified by gas chromatography-mass spectrometry

Retention time (min)	Compound	Class
18.0–19.9	Palmitic acid	SFA
22.7–23.9	Linoleic acid	UFA
31.5	10-Demethyl squalene	H
39.1	β–Sitosterol	S
39.5	Cyclolanostenol	S
40.2	β-Amyrin	S
40.7	24-Methylcyclolanostenol	S

SFA, Saturated fatty acid; UFA, unsaturated fatty acid; H, hydrocarbon; S, sterol

This trend was clearer in oxygen-delignified pulp than unbleached pulp. This result indicated that residual extractives had very different chemical structures when compared with lignin, with a more saturated structure highly resistant to acid hydrolysis. In oxygen delignification, kappa-number-contributing extractives were well removed but Klason-lignin-contributing extractives were more resistant. This was confirmed by residual extractives analysis using GC-MS as shown in Fig. 3.

The main peaks of the GC-MS chromatograms were assigned as shown in Table 2. There have been conflicting reports concerning the oxidation of residual extractives in oxygen delignification. Hrutfiord and Hopley[10] proposed an oxidation reaction mechanism for unsaturated fatty acid in oxygen delignification, whereas Holmbom[11] and Gutierrez et al.[12] insisted that there was no oxidation of residual extractives in oxygen delignification.

Oxygen is supposed to penetrate into lipophilic extractive aggregates.[11] The removal of the main extractives during oxygen delignification resulted from dissolution and dispersion of extractives under alkaline conditions and following effective washing. In oxygen delignification of Eucalyptus kraft pulp, residual extractives composition be-

Table 3. Permanganate consumption by extractives

Compound	Equivalents/mole
β-Sitosterol	2.6
Linoleic acid	12.2
Palmitic acid	0.0
Birch residual lignin[a]	9.3
Pine residual lignin[a]	11.0–11.7

[a] See Gellerstedt[13]

fore and after oxygen delignification was similar.[12] The total ion chromatogram (TIC) from GC-MS analysis (Fig. 3) clearly indicates unsaturated fatty acid oxidation in oxygen delignification. The peaks of unsaturated fatty acids were significantly decreased after oxygen delignification, but the peaks of the other extractives were unchanged. Oxygen reacts with linoleic acid to form a conjugated radical, which then reacts with the peroxy radical to form organic peroxide.[10] Organic peroxides are further oxidized in water to soluble substances and are removed in washing.

In oxygen delignification, kappa-number-contributing extractives were removed. Based on residual extractives analysis, the kappa-number-contributing extractives were mainly linoleic acid.[5] In oxygen-delignified pulp, residual extractives were mainly sterols, steryl esters, and saturated fatty acid,[5] which were expected as Klason-lignin-contributing extractives.

Simulation of lignin content determination with model extractive compounds

The contribution made by model extractive compounds to lignin content was measured using permanganate consumption (equivalent to the kappa number method) and from the precipitates formed after acid hydrolysis (equivalent to the Klason lignin method). Linoleic acid (unsaturated fatty acid), palmitic acid (saturated fatty acid), and β-sitosterol (sterol) were selected as representatives of the three different extractive types.

Linoleic acid and β-sitosterol consumed acidic permanganate. Linoleic acid consumed more permanganate than the residual lignin of birch or pine (Table 3). Permanganate consumption by β-sitosterol was significantly lower than those by the other monounsaturated compounds. α-Terpineol, which has a double bond, consumed 5.7 equivalents of permanganate per mole.[13] Because oxidation of unsaturated fatty acids was the main reaction in oxygen delignification, as shown in Fig. 3, the main extractives contributing to the kappa number quantification were unsaturated fatty acids.

The impact of model extractive compounds on Klason lignin was measured as the recovery of solid material after acid treatment (Table 4). After acid treatment, linoleic acid remained as an oily phase in solution. However, linoleic acid has a low melting point (–5°C), which allowed linoleic acid to be filtered off in aqueous solution; palmitic acid and β-sitosterol were recovered as 98% of extractives after filtration. Based on this acid treatment with model extractive

Table 4. Extractives recovery after acid treatment

Compound	Recovery (%)
β-Sitosterol	98.0
Linoleic acid	0.0
Palmitic acid	98.0

compounds, residual saturated fatty acids and sterols in pulp contributed to Klason lignin while unsaturated fatty acid did not. None of the three model compounds influenced ultraviolet spectroscopic quantification of acid-soluble lignin.

Conclusions

Sterols, steryl esters, and fatty acids were the main compounds in residual extractives from aspen kraft pulp. Unsaturated fatty acids were easily removed due to oxidative degradation in oxygen delignification. Sterols, steryl esters, and saturated fatty acids (palmitic acid) were resistant to oxygen delignification, and mainly contributed to Klason lignin determination. Linoleic acid (unsaturated fatty acid) was identified as the main extractive contributing to kappa number. The main extractives contributing to kappa number and Klason lignin were confirmed through model extractive compounds such as β-sitosterol, linoleic acid, and palmitic acid.

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