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Impact of Residual Extractives and Hexenuronic Acid on Lignin Determination of Kraft pulps

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ABSTRACT

The amount of non-lignin components in unbleached and oxygen-delignified kraft pulps and their impact on lignin determinations was investigated. The lignin analyses investigated were kappa number and Klason lignin in conjunction with acid-soluble lignin. The species investigated were loblolly pine, and aspen. The non-lignin components that impacted on lignin determination were residual extractives and hexenuronic acid in unbleached and oxygen-delignified kraft pulps.

In the hardwoods, significant amounts of extractives remained after kraft pulping and oxygen delignification. These residual extractives in the hardwood pulps had an impact on the lignin determination, more so on the acid lignin method than kappa number. Hexenuronic acid only impacts on kappa number determination both softwood and hardwood pulps, not on acid lignin. Hexeneuronic acid contributed as lignin content more in aspen than pine pulps, and more in oxygen-delignified than unbleached kraft pulps. Impact of hexenuronic acid on should be corrected both softwood and hardwood pulps for accurate kappa number.

Keywords : extractives, kraft pulps, oxygen-delignified pulps, hexenuronic acid, kappa number, Klason lignin, acid-soluble lignin, loblolly pine, aspen

1. Introduction

The correct determination of lignin is fundamental to lignin chemistry and pulping and bleaching process control. We can determine lignin content by direct measurement of the lignin or by indirect methods. Kappa number is a widely used indirect method for lignin determination in pulps. Klason lignin (Acid-insoluble lignin) with acid-soluble lignin is general method for direct lignin determination.

Kappa number is based on permanganate consumption by selectively oxidizes lignin in pulp under acidic conditions (1,2). There is a

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line ar relationship between kappa number and the Klason lignin content in chemical pulps (3,4). However, the oxidative or reductive treatment of pulp will influence whether the kappa number reflects the "true" lignin content (5).

In addition to lignin, unsaturated bond in hexeneuronic acid and extractives can react with the permanganate ion and can contribute to the kappa number (6,7). The impact on the kappa number from hexeneuronic acid in xylan was reported (8-10).

Klason lignin (11) with acid-soluble lignin (12) is a standard method for lignin determination in wood and pulps. For accurate lignin determination, solvent extraction prior to acid hydrolysis is required for extractives removal from the sample.

Organic solvent extraction before lignin determination is required for groundwood and other high-yield pulp but there is no mention for bleachable pulps.11Bleachable grade kraft pulps are typically regarded as being almost extractive-free and skipping solvent extraction before the lignin determination (5). However, significant amounts of extractives were found in aspen and birch kraft pulps.

The objective of this study was to determine that the impact non-lignin components on lignin determination. Residual extractives and hexenuronic acid was investigated as major non-lignin components which impacts on lignin determination.

2. Experimental

2.1. Wood Species

Loblolly pine (*Pinus taeda* L.) and trembling aspen (*Poplus tremuloides* M.) species were selected for the study.

Kraft Pulping, oxygen delignification and extraction of pulp were described in Shin and coworkers (13).

2.2 Kappa Number

Kappa numbers were determined according to TAPPI Test Method T236 om-99.

2.3 Acid Lignin Analyses

Acid-insoluble lignin (Klason lignin) was determined according to TAPPI Test Method T222-om-98 and acid-soluble lignin was determined according to TAPPI Useful Method UM 250.

2.4 Hexenuronic Acid Analyses

Hexenuronic acid was determined by a selective hydrolysis of hexenuronic acid groups by mercuric chloride(14).

3. Results and Discussion

3.1 Residual extractives in kraft and oxygen-delignified kraft pulps

After kraft pulping and oxygen delignification of the kraft pulps, extractives still remained in both types of pulps. The amounts of the residual extractives in the pine and aspen

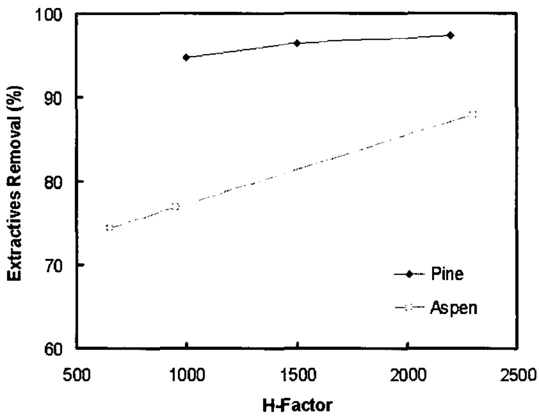

Fig. 1. Extractives removal in kraft pulping.

Table 1. Residual extractives in kraft and oxygen-delignified pulps

Samples	Extractives (%)[a]		
	Wood [b]	Kraft pulp[c]	Oxygen-delignified pulp[c]
Pine H-1000	1.92	0.21	0.11
Pine H-1500	1.92	0.15	0.05
Pine H-2200	1.92	0.12	0.05
Aspen H-650	2.47	1.09	0.52
Aspen H-900	2.47	1.02	0.50
Aspen H-2300	2.47	0.54	0.43

[a] Ethanol-benzene (1:2, vol) extraction
[b] Based on oven-dried weight of wood
[c] Based on oven-dried weight of pulp

pulps are presented in Table 1. The hardwood (aspen) pulps, as anticipated, had higher extractives contents than the softwood (pine) pulps both kraft and oxygen delignified pulps.

The percentages of the original extractives removed in the kraft pulping are shown in Fig. 1. The removal of the extractives from pine during pulping was greater than 95% while the removal from the aspen was much lower.

Hexenuronic Acid in Unbleached and Oxygen-delignified Kraft Pulps and Its Impact on Kappa Number

The amount of hexeneuronic acid in kraft pulps depends on the pulping conditions but typically hardwood kraft pulps have higher hexeneuronic acid content (60-90 μmol of hexeneuronic acid per gram of pulp) than softwood pulps (40-50 μmol of hexeneuronic acid per gram of pulp) (15,16). Not only because of the higher hexeneuronic acid content but also because hardwoods are pulped to lower kappa numbers (15~20 for hardwood vs 30~35 for softwood), the impact of hexeneuronic acid on the pulp kappa number is greater in hardwood pulps.

Hexenuronic acid contents in unbleached and oxygen-delignified kraft pulps are shown in Table 2 and 3. Aspen pulps had higher hex*enuronic acid content than those of pines.* Most of hexenuronic acid was survived after oxygen delignification. Higher hexenuronic acid content and lower initial kappa number in aspen pulps was more impact on kappa number. Due to oxygen delignification resistance of hexenuronic acid, the impact of kappa number on hexenuronic acid is more significant in oxygen-delignified pulp (Table 3).

Table 2. Hexenuronic acid in unbleached kraft pulps

Pulp	Kappa number [a]	Hexenuronic Acid (mol/g pulp)	Kappa Equivalent
AK 2300	8.4	37.5	63.0
AK 950	14.2	53.12	4.3
AK 650	22.5	50.0	94.1
PK 2200	19.7	20.96	1.7
PK 1500	23.8	21.3	31.7
PK 1000	32.8	34.77	2.8

[a] Based on extractives-free pulp

Table 3. Hexenuronic acid in oxygen-delignified kraft pulps

Pulp	Kappa number [a]	Hexenuronic Acid (mol/g pulp)	Kappa Equivalent
AO 2300	4.4	35.8	53.2
AO 950	7.0	44.16	3.5
AO 650	14.4	47.1	73.8
PO 2200	9.4	19.94	1.6
PO 1500	11.6	22.2	11.8
PO 1000	19.5	32.99	2.6

[a] Based on extractives-free pulp

3.2 Impact of non-lignin components on the kappa number of unbleachedand oxygen-delignified kraft pulps

Extractives, which remain after kraft pulping and oxygen delignification, impact the permanganate consumption during a kappa number determination. The amount of permanganate consumed depends on the degree of unsaturation in the extractive's chemical structure. The higher amount of extractives in the aspen and birch pulps contributed more to the apparent kappa number than the extractives in the pine pulps in Fig. 2.

Residual hexeneuronic acid in unbleached and oxygen-delignified kraft pulps also impacts on kappa number determination as shown in

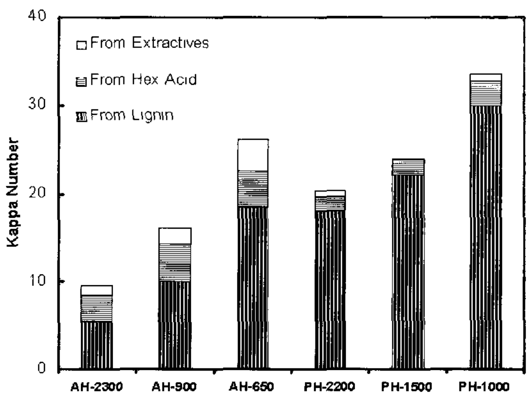

Fig. 2. Impact of non-lignin components on kappa number of unbleached kraft pulps.

Table 2 and 3. Hexeneuronic acid impacts on kappa number more aspen than pine kraft pulps, and more oxygen-delignified pulps than unbleached kraft pulps.

For aspen unbleached kraft pulps, significant portion of kappa number came from non-lignin components. Hexeneuornic acid impacted 15.7-31.6% of kappa number and residual extractives contributed 11.3-13.8% of kappa number as shown in Fig. 2. For pine unbleached kraft pulps, contribution to kappa number from non-lignin components were less significant than those of aspen. Hexeneuronic acid contributed 7.1-8.4% of kappa number and impact of residual extractives to kappa number was negligible as 0.8-3.0% of kappa number

For aspen oxygen-delignified kraft pulps, kappa number came from non-lignin components more than unbleached pulps. In oxygen delignification, lignin and residual extractives were removed. But most of hexenuronic acid was survived, which impacts more kappa number due to lower kappa number from in oxygen-delignified pulps (in Fig 3).

Hexeneuornic acid impacted 25.0-64.0% of kappa number and residual extractives contributed 5.3-12.0% of kappa number as shown in Fig. 3. For pine oxygen-delignified kraft pulps, contribution to kappa number from non-lignin components were less significant than those of aspen, as shown in unbleached

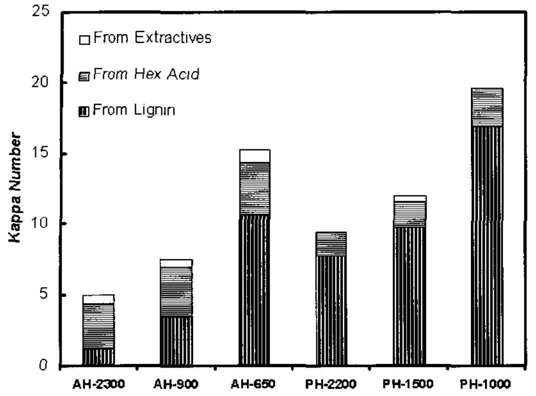

Fig. 3. Impact of non-lignin components on kappa number of oxygen-delignified kraft pulps.

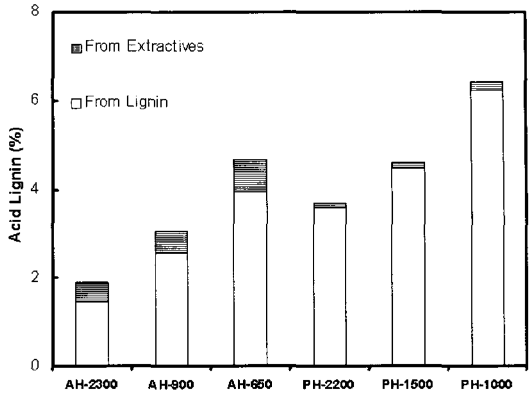

Fig. 4. Impact of non-lignin components on acid lignin of unbleached kraft pulps.

kraft pulps. Hexeneuronic acid contributed 13.3-17.0% of kappa number and impact of residual extractives to kappa number was negligible as 0.0-2.5% of kappa number

3.3 Impact of extractives on the acid lignin (Klason lignin and acid-soluble lignin) of unbleachedand oxygen-delignified kraft pulps

The contribution of extractives to the acid lignin measurements was significant for the hardwood pulps and negligible for the pine pulps (in Fig. 4). Extractives had an impact of 15-24% on the acid lignin determination for unextracted aspen unbleached kraft pulps but only 2-3% for those ofpine pulps. The impact of extractives on acid lignin measurements of wood is well known so extraction of the wood with organic solvents prior to the analysis is recommended (11). Strongly alkaline conditions in kraft pulping are, in some cases, believed to remove most of the extractives (5,17). This is essentially true for softwood kraft pulping but hardwood extractives are highly resistant to alkaline pulping especially the sterols (steroids) and steryl esters. These extractives can survive kraft pulping and remain in the pulp.

The extractives remaining after oxygen delignification of the kraft pulps also impacted the acid lignin determination (in Fig. 5). The impact on the acid lignin of aspen oxygen-delignified pulps was the equivalent of 0.25-0.59% acid lignin, lower than the contribution for unbleached hardwood kraft pulp, i.e. 0.44~0.72% acid lignin. The relative contribution of the extractives to the acid lignin of the oxygen-delignified hardwood pulps ranged from 21-42%. The impact of extractives on the acid lignin of oxygen-delignified pine kraft pulps was considerably less, the equivalent of 0.06-0.08% acid lignin, and the relative contribution ranged from *ca.* 2-5%.

3.4 Comparison of the impact of non-lignin components (Residual extractives and hexenuronic acid) on kappa number and acid lignin analysis

Compared with residual extractives and hexeneuornic acid impacting kappa number, only residual extractives interfere lignin determination based on acid lignin method. Hexenuronic acid reacts during acid lignin determination process and is converted to 2-fu-

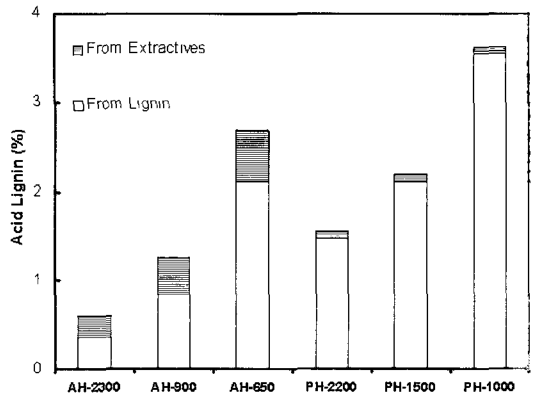

Fig. 5. Impact of non-lignin components on acid lignin of oxygen-delignified kraft pulps.

roic acid. This 2-furoic acid is well dissolved in acidic medium (not interference Klason lignin) and have no absorption in the 200-205 nm regions (distinct UV absorption with maximum absorption at 260 nm and not interfere acid-soluble lignin) (18).

Higher extractives content in aspen unbleached and oxygen-delignified pulps resulted in higher impact on acid lignin than pine pulps (in Fig 4 and 5). Acid-lignin impacting extractives were not removed well than lignin, which caused higher impact on acid lignin in oxygen-delignified pulp than unbleached kraft pulp in aspen. Impact of residual extractives on acid lignin was not significant in pine unbleached and oxygen-delignified pulps.

The residual extractives inunbleached and oxygen-delignified aspen kraft pulps had more of an impact on the acid lignin determination than the kappa number. This is the result of the chemical nature of the residual extractives, which are less unsaturated than lignin. Only compounds with structures, which can be oxidized by acidic permanganate, would contribute to the kappa number. For the acid-insoluble lignin determination (Klason lignin) extractives, which resist acid hydrolysis and are insoluble in the acidic medium would contribute to the value.

4. Conclusions

In addition to actual lignin, non-lignin components in kraft pulps contributed in lignin determination both kappa number and acid lignin methods. Hexeneuronic acid in xylan and residual extractives were impact on lignin determination.

Impact of hexeneuornic acid and extractives on kappa number of unbleached kraft pulps were more significant in aspen pulp than those of pine. Hexeneuronic acid contributed to kappa number more than residual extractives both aspen and pine pulps. Portion of kappa number from hexeneuronic acid was increased after oxygen delignification both aspen and pine pulps, which means hexeneuoric acid was highly resistance in oxygen delignification.

Impact of extractives on acid lignin of kraft pulp was more in aspenpulps than pine pulps both unbleached and oxygen-delignified kraft pulps. Portion of acid lignin from residual extractives was increased after oxygen delignification in aspen pulps.

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