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Impact of Residual Extractives in Kraft Pulps on Brightness and Color

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ABSTRACT

Residual extractives had a noticeable impact on the brightness of unbleached hardwood kraft pulps (trembling aspen). The brightness-impacting extractives were effectively removed by oxygen delignification. In addition, oxygen delignification was more effective in removing chromophores in hardwood unbleached kraft pulps than in those of softwood (loblolly pine).

The residual extractives in unbleached hardwood kraft pulps also affected the pulp color, primarily redness and the L value. These redness-related extractives in unbleached hardwood kraft pulps were also effectively removed by oxygen delignification. There were no significant color differences between untreated and solvent-extracted oxygen-delignified aspen kraft pulps. The residual extractives in unbleached and oxygen-delignified softwood (loblolly pine) kraft pulps did not have a significant impact on either brightness or pulp color.

Key words: *residual extractives, kraft pulp, oxygen-delignified pulp, loblolly pine, trembling aspen, brightness, pulp color*

1. Introduction

Cellulose and hemicelluloses are inherently white and do not affect the color of pulp. Kraft pulp has a deep brown color due to lignin structural changes in the pulping process. Oxygen delignification is an efficient delignification process step conducted prior to beginning the bleaching process. Forty to fifty percent of the residual lignin in the kraft pulp is removed; however, the brightness is not increased, which is why delignification is not considered a bleaching process. The yellowish color of the residual lignin lowers the brightness of unbleached and oxygen-delignified kraft pulps.

Bleachable-grade kraft pulps are typically regarded as being nearly extractive-free and not requiring solvent extraction prior to acid-insoluble lignin determination (1). However, the kraft pulping process cannot completely remove the extractives, and their presence results in incorrect lignin determination using both the kappa number and acid lignin methods (Klason lignin and acid-soluble lignin), especially for

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hardwood pulps (2). In the kraft pulping process, more than 90% of the extractives are removed for pine, but only 70–85% of the extractives are removed for aspen, depending on the H-factor. The residual extractives content in aspen unbleached kraft pulps has been reported as 0.5–1.1% and for oxygen-delignified kraft pulps, 0.4–0.5%.

Wood extractives are made up of small amounts of solvent-extractable organic compounds, including resin acids, fatty acids, terpenoids, steroids, and phenolic compounds. Each extractives class has different chemical properties and color. Residual extractives have been reported as having a negative impact on the brightness of mechanical pulps (3). Solvent extraction of unbleached mechanical pulp from western red cedar increased pulp brightness by 4 points. Similarly, methanol extraction of bleached pulp increased brightness by 6 points. In alkaline hydrogen peroxide bleaching of western red cedar, a portion of the residual extractives remained and affected the brightness of the resulting bleached pulp.

However, there have been no reports on the impacts of residual extractives on pulp brightness and color in kraft pulps. This study examined the influence of residual extractives in unbleached and oxygen-delignified kraft pulps on pulp brightness and color.

2. Experimental

2.1 Preparation of Kraft Pulps

Kraft pulps were prepared from loblolly pine (*Pinus taeda* L.)andtremblingaspen (*Populus tremuloides* M.) wood chips in an pulp digeste r(M/K Systems, Inc., Bethesda, MD, USA). The cooks were performed with an effective alkali charge of 15% and 18% for the aspen and the pinechips, respectively; 30% sulfidity; and a liquor-to-wood ratio of 4. The pulping temperature was maintained isothermally at 170°C (T_{max}) including a1-h heating-up period. Aseries of pulps with differen tkappa numbers was obtained by varying the H-factors for the pine (1000, 1500, and 2200) and aspen (650, 950, and 2300) cooks.

2.2 Oxygen Delignification

Oxygen delignification was performed using a 2% NaOH charge and 0.5% $MgSO_4.7H_2O$ per g oven-dried pulp. The process was conducted in a Quantum Mark IV reactor (Quantum Technologies, Twinsburg, OH, USA) at 10% consistency at 100℃ unde r0.7 MPa oxygen pressure for 1h.

2.3 Extraction of Pulps

Air-dried kraft or oxygen-delignified pulps (10 g oven-dried) were extracted as described in TAPPI Test Method T204 cm-97(4). An ethanol-benzene mixture (1:2v/v) was used as the extracting solvent. The extractives content of the wood chips was. measured using 40–60 mesh woodmeal prepared from air-dried wood chips prior to kraft pulping, using the same extraction process as for the pulps.

2.4 Brightness and Color Measurement

Brightness and color were determined according to TAPPI Test Method T452 om-98 (5) and TAPPI Test Method T527 om-94 (6), respectively, with a Brightmeter^{TM} (Technidyne Corp., New Albany, Indiana, USA)

3. Results and Discussion

3.1 Influence of Residual Extractives on Pulp Brightness

To obtain white pulp, pulps must be bleached. The brightness of pulp is measured in ISO brightness, which is expressed as a percentage of absolute whiteness using magnesium oxide as the standard. The ISO brightness measurement focuses most of the reflectance increase at the blue end of the spectrum, which is sensitive to small differences in bleaching.

In kraft pulping, almost 90% of the wood lignin is solubilized into the cooking liquor. The remaining lignin is primarily responsible for the brown color of the unbleached kraft pulp. This residual lignin is progressively removed from the pulp during the bleaching process. Extractives can influence the brightness of unbleached kraft pulp, for example, pulp from eucalyptus wood is more difficult to bleach than other hardwood pulps.

The extractives content of the aspen unbleached kraft pulp was quite high at 0.5−1.1%, which must be taken into account in the bleaching process (Table 1). The extractives contents in the aspen pulps were higher than in the pine pulps for both unbleached and oxygen-delignified kraft pulps.

As indicated in Table 2, solvent extraction of the unbleached kraft pulps resulted in a significantly greater increase in brightness for the aspen than for the pine pulps. However, solvent extraction of the oxygen-delignified pulps had little effect on pulp brightness (Table 3). Thus, it appears that the extractives affecting brightness were largely removed during the oxygen delignification process. In addition, residual extractives in the oxygen-delignified pulp had little effect on the brightness.

Interestingly, oxygen delignification of the aspen pulp resulted in a large increase in brightness (~20 points) compared to a 10-point increase for the pine pulp (Table 2,3). These results suggest that the chromophore groups in the unbleached aspen pulp were more labile to degradation than those in the pine pulp under oxygen delignification conditions. In addition, the difference in the brightness between the

Table 1. Residual extractives in kraft and oxygen-delignified pulps (2)

Samples	Extractives (%)[a]		
	Wood [b]	Unbleached 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-950	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

Table 2. Influence of solvent extraction on the brightness of unbleached aspen (AK) and pine (PK) kraft pulps

Pulps	Brightness, %		
	Un-extracted (A)	Extracted (B)	Difference (B-A)
AK 650 [a]	25.5	32.9	7.4
AK 950	30.7	38.1	7.4
AK 2300	36.1	40.2	4.1
PK 1000	22.0	24.8	2.8
PK 1500	23.9	26.3	2.4
PK 2200	24.3	27.5	3.2

[a] H factor

Table 3. Influence of solvent extraction on the brightness of oxygen-delignified aspen (AO) and pine (PO)kraftpulps

Pulps	Brightness, %		
	Un-extracted (A)	Extracted (B)	Difference (B-A)
AO 650 [a]	52.7	53.0	0.3
AO 950	58.1	58.0	-0.1
AO 2300	60.1	61.1	1.0
PO1000	33.5	33.4	-0.1
PO 1500	36.4	36.5	0.1
PO 2200	39.1	38.9	-0.2

[a] H factor

aspen and pine oxygen-delignified pulps was ~30 points. For aspen and pine unbleached kraft pulps with a similar lignin content (AK 650 and PK 2200), the a spen unbleached kraft pulp had a higher brightness and a larger brightness gain due to oxygen delignification (Table 2,3), indicating that the lignin chromophore groups in aspen respond differently to kraft pulping and oxygen delignification than those of pine.

3.2 Influence of Residual Extractives on Pulp Color

The color of pulp and paper can be visualized using the CIELAB system, in which "L" is a measure of perceived lightness, the "a" value measures the hue on the red/green axis with a positive "a" being red and a negative "a" being green, and the "b" value measures the hue on the yellow/blue axis with a positive "b" being yellow and a negative "b" being blue.

As shown in Table 4, solvent extraction of the unbleached kraft pulps resulted in a significantly greater increase in the "L" value and a decrease in the "a" value for aspen than for pine pulps. However, solvent extraction of the oxygen-delignified pulps had little effect on pulp color (Table 5). Thus, it appears that the color-related extractives were largely removed during the oxygen delignification process. In addition, residual extractives in the aspen oxygen-delignified pulp had little effect on color compared to those of the unbleached kraft pulps.

In the color comparison between solvent-extracted and un-extracted pulps, residual extractives in the aspen unbleached kraft pulps resulted in lower "L" and

Table 4. Influence of solvent extraction on the color of unbleached aspen (AK) and pine (PK) kraft pulps

Pulps	Color									
	Un-extracted (A)			Extracted (B)			Difference (B-A)			
	L	a	b	L	a	b	L	a	b	△ E*
AK 650 [a]	68.9	5.9	14.6	73.0	3.9	15.8	4.1	-2.0	1.2	4.7
AK 950	73.8	4.3	14.1	76.3	3.0	14.5	2.5	-1.3	0.4	2.8
AK 2300	76.4	3.1	12.9	77.2	2.5	13.5	0.8	-0.6	0.6	1.2
PK 1000	68.5	4.5	20.0	68.7	4.1	20.9	0.2	-0.4	0.9	1.0
PK 1500	70.4	3.6	19.9	69.6	3.6	20.0	-0.8	0.1	0.1	0.8
PK 2200	69.2	3.7	19.8	69.2	3.6	20.4	0	-0.1	0.6	0.6

Table 5. Influence of solvent extraction on the color of oxygen-delignified aspen (AO) and pine (PO)kraft pulps

Pulps	Color									
	Un-extracted (A)			Extracted (B)			Difference (B-A)			
	L	a	b	L	a	b	L	a	b	△ E*
AO 650 a	83.9	0.6	16.7	83.0	0.8	17.3	-0.9	0.2	0.6	1.1
AO 950	87.8	-0.1	14.2	87.7	-0.4	14.1	-0.1	-0.3	-0.1	0.3
AO 2300	86.8	0.6	14.9	86.6	0.2	14.6	-0.2	-0.4	-0.3	0.5
PO1000	73.3	3.1	24.1	73.4	3.5	24.4	0.1	0.4	0.3	0.5
PO 1500	76.1	2.3	23.2	75.4	2.3	23.4	-0.7	0	0.2	0.7
PO 2200	78.3	1.7	22.0	77.3	1.9	22.5	-1.0	0.2	0.5	1.1

higher “a” values (Table 4), but those in the aspen oxygen-delignified pulps did not have a significant impact on the “L” or “a” value (Table 5). Therefore, the color-impacting extractives in the aspen unbleached kraft pulps were effectively removed during the oxygen delignification process. There were no color differences between the extracted and un-extracted pulps for either unbleached or oxygen-delignified pine kraft pulps.

Interestingly, oxygen delignification of the aspen pulp resulted in a large increase in the “L” value (~10 points) compared to a 5-point gain for the pine pulp (Table 7), a similar trend to the increase in brightness (Table 2,3). In addition, the aspen pulp had a large decrease in the “a” value (2.3−3.4 points) during oxygen delignification compared to a loss of 0.6−1.7 points for the pine pulp. As noted previously, this is likely because the coloring groups in the unbleached aspen pulp were more labile to degradation than those of the pine pulp under oxygen delignification conditions. The “L” value difference between the aspen and pine oxygen-delignified pulps was ~10 points.

For aspen and pine unbleached kraft pulps with similar lignin contents (AK 650 and PK 2200), the aspen unbleached kraft pulp had a higher “L” value and a larger “L” value gain during oxygen delignification (Table 6), indicating that the lignin-coloring groups in aspen respond differently to kraft pulping and oxygen delignification than those in pine.

4. Conclusions

The residual extractives in the aspen unbleached kraft pulps affected pulp brightness and color; however, those in oxygen-delignified pulps did not. The brightness and color-impacting extractives were

Table 6. Influence of oxygen delignification on the color of aspen (AK) and pine (PK) kraft pulp (extractives-free pulps)

Pulps	Color									
	Unbleached (A)			Oxygen-delignified (B)			Difference (B-A)			
	L	a	b	L	a	b	L	a	b	△ E*
AK 650 a	73.0	3.9	15.8	83.0	0.8	17.3	10.0	-3.1	1.5	10.6
AK 950	76.3	3.0	14.5	87.7	-0.4	14.1	11.3	-3.4	-0.4	11.8
AK 2300	77.2	2.5	13.5	86.6	0.2	14.6	9.4	-2.3	1.1	9.7
PK 1000	68.7	4.1	20.9	73.4	3.5	24.4	4.7	-0.6	3.5	5.9
PK 1500	69.6	3.6	20.0	75.4	2.3	23.4	5.8	-1.3	3.4	6.8
PK 2200	69.2	3.6	20.4	77.3	1.9	22.5	8.1	-1.7	2.1	8.5

successfully removed by oxygen delignification. The residual extractives in the pine kraft pulps did not affect pulp brightness or color either in the unbleached or oxygen-delignified kraft pulps.

Based on extractives-free unbleached kraft pulps, chromophore groups in the aspen pulps were more labile to degradation than those of the pine pulps under oxygen delignification conditions. The brightness gain due to oxygen delignification was 20 points for aspen pulps compared with only 10 points for pine pulps. For color, the "L" value increased 10 points for aspen pulps, but only 5 points for pine pulps due to oxygen delignification. The aspen pulps had a greater decrease in the reddish color (greater decline in the "a" value) and a lower increase in the yellowish color (smaller increase in the b value) than the pine pulps during oxygen delignification.

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