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The Fate of Aspen Extractives in Kraft Pulping and Oxygen Delignification

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ABSTRACT

The compositions of residual extractives in woodmeal, unbleached and oxygen-delignified aspen kraft pulps were investigated with gas chromatography(GC) and gas chromatography-mass spectrometry (GC-MS) with focus on fate of extractives in kraft pulping and oxygen delignification.

Steryl esters and shorter retention time (shorter than palmitic acid) extractives were main extractives in aspen woodmeal. Shorter retention time extractives were well removed in kraft pulping. Sterol esters were hydrolyzed to sterols and fatty acids. Sterols and fatty acids were two major extractives classes in unbleached kraft pulps. Linoleic acid was main fatty acids in unbleached pulps compared with palmitic acid which is generally found in aspen woodmeal.

Sterolsand fatty acids were also two major extractives classes in oxygen-delignified kraft pulps. However, linoleic acid was well removed in oxygen delignification.

Keywords : *extractives, kraft pulps, oxygen-delignified pulps, palmitic acid, linoleic acid, β-sitosterol, aspen, sterols, steryl esters, fatty acids*

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1. Introduction

Kraft pulping has been the most dominant chemical pulping process. Primary advantages of this system are its affordability to rawmaterial usage (specially high extractives containing wood species), high pulp strength and simplicity of chemical recovery.

In contrast to difficulties in extractives removal in mechanical pulping or acid sulfite pulping, extractives are well removed during kraft pulping. Strong alkaline condition in black liquor renders the ionization of phenolic hydroxyl group in lignin fragments and phenolic extractives, and carboxylic acid group in resin and fatty acids. Ionized extractives were well dissolved in black liquor and removed from pulp with black liquor drainage and following washing stages.

Residual extractives after kraft pulp washing bring pitch problems in kraft mill. Introduction of Zero Effluent concept is more sensitive in residual extractives in washed kraft pulps. Difficulties in extractives removal in hardwood kraft mill were reported (1). Neutral and unsaponifiable materials with small percentages of resin and fatty acids were present in organic solvent extract from the pitch deposit.

Oxygen delignification also can remove a substantial fraction of lignin after kraft cooking using oxygen and alkali. High shear mixing in medium consistency oxygen delignification process assists extractives removal with exposing the extractives to alkaline reaction medium.

We reported that the residual extractives contents in pine and aspen kraft pulps (2). And there were significant amounts of residual extractives in aspen pulps but not in pine pulps. These residual extractives in aspen pulps affect on lignin determination both kappa number and acid lignin basis. Kappa number-impacting extractives were well removed but acid lignin-impacting extractives were resistant in oxygen delignification.

We investigated the extractives in woodmeal, unbleached and oxygen-delignified kraft pulp with focus on fate of extractives in kraft pulping and oxygen delignification with gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

2. Experimental

2.1 Kraft pulpingand oxygen delignification

Kraft pulps were prepared from the trembling aspen (Poplus tremuloides M.) wood chips in an M & K digester. The cooks used an effective alkali charge of 15 and 30% sulfidity, and liquor-to-wood of 4. Pulping temperature was maintained isothermally at 170℃ (Tmax) including one h of the heating up period. A series of pulps with different kappa number was obtained by varying the H- 650 and 2300.

Oxygen delignification used a 2% NaOH charge, and 0.5% $MgSO_4 \cdot 7H_2O$ based on oven-dried pulps. It was conducted in a Quantum Mark IV reactor at 10% consistency, and at 100℃ under a 90 psi of O_2 for one h.

2.2 Extractives analysis

Samples of air-dried wood meal (5 g), kraft and oxygen-delignified pulps (10 g) were extracted as described in TAPPI Test Method T204 cm-97 (3). An ethanol-benzene mixture (1:2, V/V) was used as the extracting solvent. After Soxhlet extraction, the extract was concentrated in a rotary evaporator to a volume of 5 mL. The resulting mixture was kept in a refrigerator, and used directly without a prior

derivatization for the GC analysis.

After Soxhlet extraction, the solvent in the extraction flask was partially evaporated in a reduced pressure rotary evaporator to a volume of 5 mL. This concentrated was kept in a refrigerator and used directly injected for GC analysis without a prior derivatization.

2.2.1 Gas chromatography

A Hewlett-Packard HP 5890 gas chromatograph equipped with a split-splitless injector and a flame ionization detector (FID) system was used (Hewlett-Packard, CA, USA). The injector and the detector temperature were set at 250℃ and 330℃, respectively. Sample volumes of 2 L were injected in the splitless mode. Nitrogen was used as the carrier gas.

For the medium length capillary column method, a capillary column of DB-XLT (0.25 mm I.D., 0.25 m film thickness, 15 m) from J&W scientific was used. The temperature program employed was an initial oven temperature at 100℃ for two min, ramp at 10℃/min, to 330℃, and hold at 330℃ for 15 min.

For analysis of the steryl fatty acid esters, a short capillary column of DB-5 (0.25 mm I.D., 0.25 m film thickness, 2 m) from J&W scientific was applied. The temperature programs was run at 100℃ for 2 min and then raised to 330℃ at 30℃/min, and then kept isothermally for 15 min.

2.2.2 Gas Chromatography-Mass Spectrometry (GC-MS)

The GC-MS analyses were performed on a Hewlett-Packard HP 5989B Gas Chromatography/Mass Spectrometer (GC/MS). The capillary column used was a DB-XLT (0.25 mm I.D., 0.25m film thickness, 15m) from J&W scientific. The temperature program employed was as follows: initial oven temperature at 100℃ for 2 min, ramp at 5℃ /min, to 330℃ and hold isothermally for 15 min. The injection and detector temperatures were the same as indicated earlier in analysis in GC. The mass spectra were obtained by an Electron impact (EI) ionization mode at electron beam energy of 70 eV.

3. Results and Discussion

3.1 Determination of extractives

The extractive mixture isolated was subjected directly to the GC and GC-MS analyses without a prior derivatization using higher temperature resistant capillary columns (4). Two types of columns were used in this study. A short capillary column of DB-5 (2 m) was employed to quantify the steryl esters, and a medium capillary of DB-XLT (15 m) was used to estimateall other components. The short column analysis was intended to overcome reported difficulties in detection of the steryl esters and triglycerides with a medium length capillary (5). Both in the GC-FID and GC-MS analyses, the final oven temperature was set at 330℃, which was sufficient for determining the sterols and steryl esters.

Figure 1 illustrates the gas chromatogram of a short capillary column analysis for residual extractives from an O_2-delignified aspen kraft pulp. The steryl ester fraction was analyzed based on authentic compounds of heptadecanoic acid, -sitosterol and cholesteryl oleate for fatty acids, sterols and steryl esters, respectively. A test run with authentic cholesteryl oleate indicated that this compound was partially degraded to cholesterol and oleic acid (9-octadecenoic acid). A correction factor was then used to adjust for a partial degradation of steryl fatty acids to sterols and fatty acids in

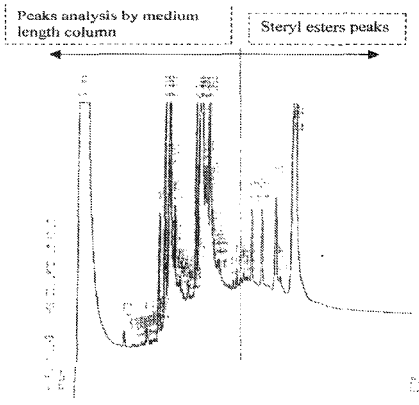

Fig. 1. A short capillary column GC chromatogram for residual extractives from an O_2-delignified aspen kraft pulp.

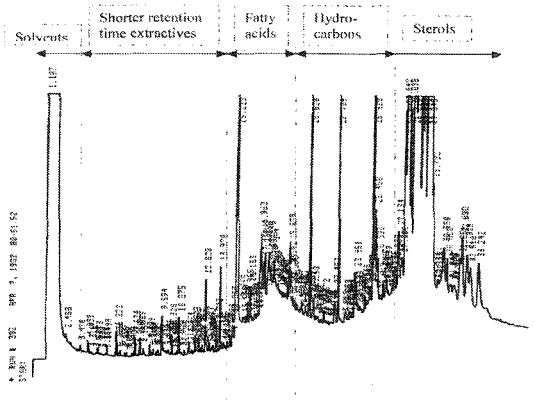

Fig. 2. A medium capillary column GC chromatogram for residual extractives from an O_2-delignified aspen kraft pulp.

the yield determination.

Figure 2 shows the gas chromatogram of a medium capillary column analysis for residual extractives from an O_2-delignified aspen kraft pulp. As indicated, the chromatogram can be grouped into four major fractions based on the retention time (RT): shorter RT extractives (than palmitic acid), fatty acids, hydrocarbons, and sterols. It should be noted that most of the GC peak areas (81.2%) matched well with peaks in the GC-MS analysis.

In this study, four assumptions were made for quantitative estimation of the extractives:

1. All the extractives isolated can be detected by the combined short and medium capillary analyses.
2. The GC response factor in analyses was assumed being the same within the same class of compounds. Authentic compounds of stigmasterol for the sterol, palmitic acid for the fatty acid, and cholestryl linoleate for the steryl esters in the calibration and yield determination.
3. The shorter RT fraction (extractives with shorter retention time than palmitic acid) was a mixture of hydrocarbons, fatty acids, and unclassified compounds. The response factor for these components was assumed being the same as for sterols.
4. Those GC-FID peaks, which could not match with the GC-MS peaks, were classified as the unknown and estimated using the same response factors as sterols.

3.2 Influence of kraft delignification

As indicated in Tables 1 and 2, kraft delignification not only reduced the residual extractive content of aspen kraft pulps but also altered its chemical composition. This suggests that the degradation and removal of individual extractives are not uniform in kraft cooks. The noticeable changes are outlined in the following.

First, the content of steryl esters decreased steadily with kraft delignification. A 65% reduction was shown for the most extended cook (H2300). Secondly, the shorter RT fraction also reduced considerably with kraft delignification, and a 94% reduction was observed for the most extended cook (H2300).

Thirdly, the sterol fraction increased

Table 1. Composition of extractives in aspen wood and kraft pulps

Class	Composition of Extractives				
	Wood	Unbleached pulp		Oxygen-delignified pulp	
		H-650	H-2300	H-650	H-2300
% Extractives in wood or pulp	2.5	1.1	0.5	0.5	0.4
Steryl esters1	31.0	18.6	10.4	18.8	3.6
Shorter RT2 extractives	30.5	8.5	1.9	2.0	4.6
Sterols	16.1	35.7	45.5	45.5	56.6
Hydrocarbons	5.8	1.8	5.4	7.4	5.9
Fatty acids	12.0	20.6	22.6	11.9	8.7
Phenolic	0.7	3.4		2.6	0.9
Unclassified peaks	0.1	2.4	4.1		1.7
Not matched with GC-MS peak	3.8	9.0	9.9	11.0	18.4
Subtotal from medium column GC	69.0	81.4	89.6	81.2	96.4
Total	100.0	100.0	100.0	100.0	100.0

[1] steryl esters content from short-column GC analysis
[2] RT : retention time

Table 2. Sterols and fatty acids in aspen wood and kraft pulps

Class	Composition of Extractives				
	Wood	Unbleached pulp		Oxygen-delignified pulp	
		H-650	H-2300	H-650	H-2300
Sterols	16.1	35.7	45.5	45.5	56.6
10-demethylsqualene	0.7	0.92	0.7	2.1	1.0
β-sitosterol	3.0	7.6	6.8	11.3	9.9
β-amyrin	0.7	3.0	6.2	4.1	
Cyclolanostenol	0.7	1.7			1.2
Viminalol	0.8	4.0	4.1	4.8	5.2
Stigmastadienone	1.9	3.7			
24-methyl cyclolanostenol	3.0	7.3	14.7	13.0	14.5
Fatty acids	12.0	20.6	22.6	11.9	8.7
Hexadecanoic acid	8.7	3.1	3.3	4.0	3.0
9,12-octadecadienoic acid	0.8	16.5	15.5	4.7	5.5
Ethyl linoleate		0.6	1.5		

considerably with kraft delignification resulting in a 184% increase for the most extended cook (H2300). It is the major extractive in the aspen kraft pulps. As indicated in Table 2, all the

individual components were significantly higher in kraft pulps than in the wood sample. This suggests that most of the sterol components were also generated during the kraft cooking, especially in case of 24-methyl cyclolanostenol.

Fourthly, the fatty acid fraction showed a significant increase with kraft delignification, and the major components identified were palmitic acid (hexadecanoic acid) and linoleic (9,12-octadecadienoic) acid. These two acids behaved differently in kraft cook showing a lower palmitic acid and a higher linoleic acid content. An increase of the latter acid was likely resulted from alkaline hydrolysis of the triglycerides and steryl esters in cooking of aspen wood (6).

Finally, the hydrocarbon content of kraft pulps seems to be comparable to that aspen wood, except a significantly lower value for the high kappa number pulp (H 650).

3.3 Influence O_2 delignification

As indicated in Table 1, the major types of extractives in O_2-delignified aspen kraft pulps were sterols, fatty acids, steryl esters and hydrocarbons. Thus, O_2 delignification not only reduced the residual extractive content of kraft pulps, and also had noticeable effects on individual extractive components (Table 2).

It is evident that O_2 delignification increased the proportion of sterols in the residual extractives (45.5~56.6% vs. 35.7~52.6%). However, the proportion of fatty acids was significantly reduced after the O_2 delignification, especially for the 9,12-octadecadienoic (linoleic) acid. In a previous report on the reaction of the latter acid in oxygen delignification (7), the unsaturated groups were found being labile to undergo auto-oxidation leading to fragmentation. In case of hexadecanoic (palmitic) acid, its proportion was little affected by oxygen delignification.

On the hydrocarbon fraction, its proportion in residual extractives was increased after O_2 delignification (5.9~7.4%) as compared to the unbleached pulps (1.8~5.4%). Since most of the hydrocarbon products in oxygen-delignified pulps were not identified, it is difficult to discuss the fate of individual components.

The apparent proportion of steryl esters in residual extractives of aspen kraft pulps was little affected by oxygen delignification, except a significant reduction was shown for the extended cooked sample (H2300). The latter indicated an extensive hydrolysis of steryl fatty acid esters during the oxygen delignification.

4. Conclusions

Both the kraft pulping of aspen wood and the subsequent oxygen delignification has a considerable impact on the composition of residual extractives. Steryl esters and shorter retention time (shorter than palmitic acid) extractives were main extractives in aspen woodmeal. Shorter retention time extractives were well removed in kraft pulping.

The key reaction in kraft cook was the hydrolysis of steryl esters and easy removal of shorter retention time extractives. Sterols and fatty acids (mainly linoleic acid) were two major extractives classes in unbleached kraft pulps. In oxygen delignification, the oxidative degradation of unsaturated extractives was significant as in case of linoleic acid. Interestingly, a significant amount of steryl esters survived the kraft cook and even after the oxygen delignification.

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