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Why are Aspen Extractives More Resistant in Kraft Pulping Than Pine Extractives?*1

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ABSTRACT

We investigated why aspen extractives are more resistant in kraft pulping than pine extractives. Residual extractives content in aspen kraft pulps were 0.5~1.1% compared with 0.1~0.2% in pine pulps. This different response arises from the different composition of extractives in wood chips. Resin acids in pine were almost completely removed in kraft pulping but those are not existence in aspen. Slower saponification of aspen steryl esters resulted from different chemical structure of aspen steryl esters. Main sterols in aspen steryl esters were 24-methyl cyclolanostenol which was highly resistant to alkaline hydrolysis with its characteristic steric hindrance. Sterols in aspen were not well removed in kraft pulping. The relative composition of sterol in aspen kraft pulps was increased with increasing pulping time. The presence of fatty acids in aspen kraft pulps is considered to unusual. Fatty acids in alkaline are supposed to be well ionized and removed well in the washing stage. Nevertheless, there were significant amount of fatty acids remaining in aspen kraft pulps.

Keywords : extractives, kraft pulps, aspen, pine, 24-methyl cyclolanostenol, palmitic acid, linoleic acid, saponification, steryl esters, sterols, fatty acids

1. INTRODUCTION

In pulp and paper industry, extractives cause problems known as pitch trouble (Allen, 1978). Pitch formed on equipment contains hydrophobic wood extractives (Mutton, 1962), which are mainly fatty acids, resin acids, sterols, steryl esters, and glycerides (Sjöström, 1993) with each class of extractives responding differently in the pulping process.

In the neutral or acidic pulping condition, hydrophobic extractives are difficult to remove, which hinder high extractives containing wood species as a pulping resource. Chip seasoning is one of the solutions for the neutral or acidic pulping for high extractives containing wood species. During chip storage, glycerides are hydrolyzed and oxidized, which decrease the extractives

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content of wood chips. In the alkaline pulping process, the ester linkages in steryl esters and glycerides are hydrolyzed to fatty acids and sterols/glycerols. Carboxyl groups in fatty and resin acid are ionized and dissolved in alkali. These ionized fatty and resin acids are not only well dissolved but also assisted in removing other neutral extractives acting as surfactants. Even high extractives containing wood species can be used in alkaline pulping.

However, pitch trouble in aspen and birch kraft mill has been reported in the winter season with difficulties in debarking (Allen, 1988). Although aspen is one of the high extractives containing hardwood species, its extractives content is similar or less extractives than that of softwood species (Hafizoglu, 1989). Extractives content, therefore, cannot explain the pitch trouble in aspen kraft pulping. We also reported significant amounts of residual extractives in aspen and birch kraft pulps but not in pine pulps (Shin *et al.* 2004). In this study, we investigated why aspen wood extractives are more resistant in kraft pulping than pine wood extractives.

2. EXPERIMENTAL

2.1. Kraft Pulping

The kraft pulps were prepared from the loblolly pine (*Pinus taeda* L) and trembling aspen (*Poplus tremuloides* M.) wood chips. The cooks were conducted in an M&K digester using a liquor-to-wood ratio of 4, at a maximum temperature of 170°C including 1 h of temperature rise to the target temperature and with air - dried chip, 400 g of oven-dried weight equivalent. The effective alkali charges were 15% for aspen and 18% for pine cook, respectively and the sulfidity was all at 30% as Na_2O basis. A series of different level of delignification with different kappa number was obtained by varying the H-factors; for pine (1000 and 2200), and aspen (650 and 2300) cooks.

2.2. Extraction of Pulps

Air-dried kraft pulp (10 g, oven-dried basis) was extracted as described in TAPPI Test Method T204 cm-97. Ethanol-benzene (1:2, v/v) was used as the extracting solvent.

2.3. Extraction of Woodmeal

Air-dried wood chips were milled in a Wiley mill to 40~60 meshes. A sample of air-dried wood meal (5 g oven-dried basis) was similarly extracted for kraft pulps.

2.4. Extractives 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.

2.5. 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°C and 330°C, respectively. Sample volumes of 2 $\mu\ell$ 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 μm film thickness, 15 m) from J&W scientific was used (Fernadez *et al.*, 2001). The temperature program employed was an initial oven temperature at 100°C for two min, ramp at 10°C/min, to 330°C, and hold at

330°C 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 μm film thickness, 2 m) from J&W scientific was applied (Gutierrez *et al.*, 1998). The temperature programs was run at 100°C for 2 min and then raised to 330°C at 30°C/min, and then kept isothermally for 15 min.

2.6. 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., 0.25 μm film thickness, 15 m) from J&W scientific. The temperature program employed was as follows: initial oven temperature at 100 °C for 2 min, ramp at 5°C/min, to 330°C and hold isothermally for 15 min. The injection and detector temperatures were the same as indicated earlier in the 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. Extractives Removal in Kraft Pulping

Ether-soluble extractives content in loblolly pine was 2.0% based on fresh cut wood (Zinkel, 1975). Ether-soluble extractives content in trembling aspen wood was reported as 1.0~2.7% (Mutton, 1958). Acetone-soluble extractives content in trembling aspen was 2.1% (Peng *et al.*, 1999).

Air-dried (or seasoned) chips prepared for kraft pulping differed from living standing trees in the composition and contents of extractives.

Table 1. Extractives removal in kraft pulping

Sample	Extractives (%)[a]		Extractives
	Wood[b]	Kraft Pulp[b]	removal (%)
Pine H-1000	1.92	0.10	94.8
Pine H-2200	1.92	0.05	97.4
Aspen H-650	2.47	0.63	74.5
Aspen H-2300	2.47	0.30	87.9

Note: H denotes H-factor.
[a]: ethanol-benzene (1:2, v/v) extraction
[b]: based on oven-dried weight of wood

Most of wood extractives analyses are based on the standing trees. This research, however, was focused on the behavior of extractives in kraft pulping. Extractives content was 1.9% for loblolly pine and 2.5% for trembling aspen with ethanol-benzene (1:2, v/v) extraction.

The percentages of the original extractives removed in the kraft pulping are shown in Table 1. The extractives removal for loblolly pine in kraft pulping was greater than 95% whereas the removal for the aspen was much lower. The higher extractives removal for the pine may follow from the different extractives composition of the wood. In ether-soluble extractives analysis, 98.5% of extractives were recovered in black liquor, which means that in kraft pulping of loblolly pine, most of extractives are dissolved (Zinkel, 1975).

3.2. Comparison of Aspen and Pine Wood Extractives

Detail of extractives analysis steps was described in Shin and Lai (2005). Based on extractives analysis with GC and GC-MS, there were several differences between aspen and pine wood extractives (in Table 1). Resin acids were the main extractives in pine but were not detected in aspen wood extractives (Douek and Allen, 1978). Resin acids were well removed in

Table 2. Extractives in pine and aspen woodmeal

Class	% FID peak area	
	Aspen	Pine
Steryl esters from short column GC	31.0	12.3
Lower RT[1] hydrocarbons	30.5	25.6
Sterols	16.1	14.5
10-demethylsqualene	0.7	
β-sitosterol	3.0	
Stigmastadienoine	1.9	
24-methyl cyclolanostenol	3.0	
Beta-amyrin	0.7	
Cyclolanostenol	0.7	
Viminalol	0.8	
Hydrocarbons	5.8	0.3
1-dotriacontanol	0.3	
1-eicosene	< 0.1	
Fatty acids	12.0	6.0
Palmitic acid	8.7	2.5
Lineolic acid	0.8	
Oleic acid		1.4
Resin acid		20.8
Phenolic	0.7	
Unclassified peaks	< 0.1	0.2
Not matched with GC-MS peak	3.8	23.2
Subtotal of medium column GC	69.0	87.7
Total	100.0	100.0

[1] RT: retention time

kraft pulping. The removal of neutral extractives in the pulp washing is highly dependent on soap solubility, micelle formation and colloidal stability (Ström *et al.*, 1990). The maximum solubility of soap and neutral extractives occurs in mixed oleate/abietic solution (1:1-2:1 by weight). Therefore, fatty acids and resin acids in pine were more favorable for extractives removal than were fatty acids in aspen.

Steryl esters content in woodmeal was higher in aspen (31.0%) than pine (12.3%). Sterol esters, one of the main hydrophobic extractives in eucalyptus wood (Gutierrez *et al.*, 1999), were not extensively hydrolyzed in kraft pulping (Gutierrez *et al.*, 2001). So the higher steryl esters content in aspen wood led to higher residual extractives in aspen kraft pulp than that of pine. Unmatched peak between GC and GC-MS in woodmeal extractives was higher in pine (23.2%) than aspen (3.8%).

3.3. Different Extractives Composition of Pine and Aspen Kraft Pulps

Steryl esters content in woodmeal was higher in aspen (31.0%) than in pine (12.3%) (Table 2). In kraft pulping, alkaline hydrolysis of steryl esters was faster in pine than in aspen. Steryl esters were reported as major hydrophobic extractives in aspen kraft pulp (Peng *et al.*, 1999). Steryl ester content in pine kraft pulps were 2.4~3.6% compared with 10.5~18.6% in aspen pulps. Steryl esters content was decreased with increasing pulping due to extended alkaline hydrolysis of steryl fatty acid ester linkages. Alkaline hydrolysis of steryl esters was slower in aspen than in pine because of different steryl esters linkages (Paasonen, 1967). In aspen, 24-methyl lanostenol is the one of the main sterols in steryl esters linkage, which is highly resistant to alkaline hydrolysis. Steric hindrance caused by the cyclopropane ring makes the hydrolysis of the ester linkage difficult. Aspen kraft pulps had a higher percentage of sterols and fatty acids content than did woodmeal as a result of the hydrolysis of steryl esters to sterols and fatty acids.

The GC and GC-MS analysis method was not effective in pine extractives analysis. Twenty percent of the GC peak in pine woodmeal extractives did not show up in total ion chromatogram (TIC) in GC-MS analysis. Forty

Table 3. Extractives composition of woodmeals and kraft pulps in aspen and pine

Class	Composition of Extractives (%)					
	Aspen			Pine		
	AW	AK650	AK2300	PW	PK1000	PK2200
Extractives Content (%) [a]	2.47	1.09	0.54	1.92	0.21	0.12
Steryl esters	31.0	18.6	10.5	12.3	3.6	2.4
Lower RT extractives	30.5	8.5	1.9	25.6	9.8	9.0
Sterols	16.1	35.7	45.6	14.5	16.0	15.3
Hydrocarbons	5.8	1.8	5.4	0.3	15.8	16.8
Fatty acids	12.0	20.6	22.6	6.0	7.7	14.9
Phenolic	0.7	3.4			0.9	0.9
Resin acid				20.8	0.2	0.6
Unclassified peaks	0.1	2.4	4.1	0.2	2.4	2.2
Not matched*	3.8	9.0	9.9	20.3	43.6	39.9
Total	100.0	100.0	100.0	100.0	100.0	100.0

A: aspen, P: pine, W: wood meal, K: unbleached pulp, number: H-factor for kraft pulping

*: not matched GC peaks with GC-MS peaks

percent of the GC peak in residual extractives in pine kraft pulp was not matched in the TIC in GC-MS analysis. In case of pine extractives analysis, other analytical method should be used for getting more information on unmatched peaks.

Resin acids were one of main extractives in pine woodmeal, but were almost completely removed in kraft pulping. Resin acids were not detected in extractives of aspen woodmeal or kraft pulps.

Woodmeal and pulp extractives in aspen had different fatty acid compositions. In woodmeal extractives, palmitic acid (or hexadecanoic acid) was the main fatty acid. However, in residual extractives in aspen kraft pulps, linoleic acid was the main fatty acid. Linoleic acids existed in wood as combined acids (ester linkage with glycerols or sterols). In kraft pulping, these ester linkages are broken down to free acids and sterols/glycerols. In pine, palmitic acid and oleic acid were presented in both wood meal and kraft pulp extractives.

Based on extractives analysis of aspen kraft pulp from pulp mill, 0.84% of residual extractives remained washed unbleached pulp, with fatty acids representing of twelve percent of residual extractives (Chen *et al.*, 1995). In this study, fatty acids were one of the main classes of extractives, making up of twenty percent of the residual extractives in aspen pulp (Table 3). The presence of fatty acids in alkaline pulps is unusual. In strong alkaline black liquor, fatty acids should be ionized as carboxylate and dissolve into black liquor. In loblolly pine kraft pulping, most of the fatty acids in wood chips were dissolved in black liquor (Zinkel, 1975).

Aspen woodmeal and kraft pulp extractives had different sterol compositions. The percentage of sterols in extractives increased in pulp to 35.7~45.6% compared with 16.1% in woodmeal. The main sterols in aspen pulps were β-sitosterol and 24-methyl cyclolanostenol compared with β-sitosterol and stigmastadienone in

Table 4. Composition of sterols and fatty acids in aspen wood and kraft pulp residual extractives

Class	Composition of Extractives (%)		
	AW	AK 650	AK 2300
Sterols	16.1	35.7	45.6
10-demethylsqualene	0.7	0.9	0.7
β-sitosterol	3.0	7.6	6.8
β-amyrin	0.7	3.0	6.2
Cyclolanostenol	0.7	1.7	
Viminalol	0.8	4.0	4.1
Stigmastadienone	1.9	3.7	
24-methyl cyclolanostenol	3.0	7.3	14.7
Lanostenol			5.4
Fatty acids	12.0	20.6	22.6
Palmitic acid	8.7	3.1	3.3
Linoleic acid	0.8	16.5	15.5

A: aspen, W: wood meal, K: unbleached pulp, number: H-factor for kraft pulping

Table 5. Composition of sterols and fatty acids in pine wood and kraft pulps residual extractives

Class	Composition of Extractives (%)		
	PW	PK 1000	PK 2200
Sterols	16.0	16.0	15.3
10-demethylsqualene		3.1	5.3
β-sitosterol		5.0	3.7
Stigmastadienoine		5.8	2.7
Fatty acids	6.9	7.7	14.9
Palmitic acid	2.5	5.1	4.7
Linoleic acid	1.4	1.4	7.8

P: pine, W: wood meal, K: unbleached pulp, number: H-factor for kraft pulping

pine kraft pulps (see Table 4). In aspen H-650 and H-2300 pulp (H-factor 650 cook and H-factor 2300 cook) extractives analysis, β-amyrin and 24-methyl cyclolanostenol content were increased with increasing pulping time. This meant that these two sterol formed steryl esters linkage resisted in alkaline hydrolysis. For pine, there was no difference between woodmeal and pulp extractives in terms of the percentage of sterols (see Table 5).

4. CONCLUSIONS

Resin acids were the main class of extractives in pine woodmeal and were well removed in kraft pulping. Not only were they well dissolved in alkali but they also assisted in removing other neutral extractives by acting as surfactants. The lack of resin acids in hardwood would be one of reasons for the poor response in kraft pulping.

Aspen and pine had different types of steryl esters. Aspen steryl esters were highly resistant to kraft pulping compared with the easily hydrolyzed pine steryl esters. In aspen, 24-methyl cyclolanstenol resisted saponification due to the presence of two methyl groups in the C-4 of cyclolanostenol, which makes the hydrolysis of ester linkage more difficult.

The main fatty acid in aspen woodmeal was palmitic whereas linoleic acid was the main fatty acid in aspen kraft pulps. Linoleic acid came from the alkaline hydrolysis of triglycerides or steryl esters. It is unusual to find high fatty acids content in aspen pulp. Fatty acids are supposed to dissolve well in black liquor and be removed in pulp washing. But fatty acids were one of the main classes of extractives in aspen kraft pulps.

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