

DERESINATION OPTIONS IN SULPHITE PULPING

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Three methods for improved deresination of sulphite pulps were evaluated, namely, alkaline washing, enzyme treatment, and pulp fractionation. Alkaline washing appears to come at a high cost, because caustic is expensive and affects cellulose chain length, as indicated by lower viscosity of the pulps. Thus this is not a viable option for pulps that are sensitive to changes in viscosity. Enzyme treatment did not completely degrade the glycerides under the mill conditions used. Fibre fractionation studies showed that the fines fractions contained 8 to 13 times more residual lipophilic extractives than the whole pulps. Removing this fraction, which represents only a small percentage of the whole pulp, could reduce by about a half the amount of lipophilic extractives in the remaining pulp. Thus pulp fractionation appears to be a viable option to achieve further deresination of sulphite pulps.

Keywords: Extractives; Pitch; Enzymes; Fractionation; Alkaline washing; Sulphite; Dissolving pulps

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INTRODUCTION

Lipophilic extractives are wood resin compounds that are comprised of resin acids, fatty acids and esters, fatty alcohols, hydrocarbons, waxes, sterols, sterol esters, glycerides, ketones, and other oxidized compounds (Ekman and Holmbom 2000). These compounds, which are non-polar in nature, may easily adhere to hydrophobic surfaces of paper machines and build up to form pitch deposits. The extractives exist in different forms depending on the pulp or papermaking process. For example, fatty acids, glycerides, and sterols are predominant in mechanical and sulphite processes, whereas the fatty acids and glycerides are saponified in alkaline processes to form soluble sodium soaps and insoluble tacky soaps of multivalent metal ions (Back and Allen 2000).

Sulphite pulps contain higher amounts of extractives compared to kraft pulps, as they are made under acid conditions and not alkaline conditions that dissolve and break down the wood resin. Consequently, these pulps tend to exhibit production and quality issues attributed to wood resin. For example, when making rayon, costly spinnerets have to be changed much more frequently when the dissolved cellulose comes from pulp containing a high content of resin extractives (Mouyal 2005). Also, extractives in pulps destined for pharmaceutical grades can cause objectionable taste and olfactory odours due to degradation and rancidity of the extractives. Consequently, sulphite mills expend significant efforts in time, effort, and money to reduce the amounts of residual extractives

in their pulps.

A variety of methods and procedures are used to reduce the amount of residual lipophilic extractives in finished sulphite pulps. They include wood or chip seasoning, good brownstock washing, use of Frotapulpers, and dispersants that help in washing out the extractives (Back and Allen 2000). Wood seasoning is expensive, as it ties up capital and also results in loss of wood (1.5-2% for spruce). Frotapulpers are a kind of blender where caustic is added to the pulp at high consistencies (~28%). The pulp is then subjected to shearing and kneading forces in the form of pulsating pressure loads, which results in deresination of the pulp. The most effective deresination surfactants are nonylphenol ethoxylates (NPEs). Unfortunately, NPEs have been implicated as estrogen mimics (Environ. Can. 2006; Guenther et al. 2002; Health Canada 2006) and, hence, their continued use is no longer desirable. So far it appears that there are no other surfactants that are as effective as NPEs in achieving low-extractives content in sulphite pulps. To make matters worse, it is now difficult for mills to obtain seasoned wood or chips due to shortage of wood fibre. Consequently, mills often have to cope with fresh chips that have high levels of lipophilic extractives. Thus, the industry is continually looking for other methods of reducing the extractives. Three methods for improved deresination of sulphite pulps were evaluated, namely, alkaline washing, enzyme treatment, and pulp fractionation.

Alkaline Washing

Since sulphite pulps are made under acidic conditions in the digester, the components of their lipophilic extractives are in the acid form (for example, resin and fatty acids are protonated) and consequently are not easily removed during washing. This is in direct contrast to kraft pulping where the alkaline conditions facilitate removal of the extractives in the washing and thickening stages. This is because the extractives are present as water-soluble sodium soaps that are easily removed during the washing stages. Alkaline washes and higher temperatures have been advocated as effective measures for deresination (Back and Allen 2000). Consequently, these measures were explored to ascertain if they could be viable options for effective deresination of sulphite pulps.

Enzyme Treatment

Analysis of the composition of residual lipophilic extractives in final sulphite pulps showed that the major components that could be analysed by GC were glycerides and steryl esters (Sitholé et al. 2006). This indicates that any deresination options contemplated to further reduce the extractives should target these compounds. Lipase enzymes have been reported to be effective in removing these compounds from mechanical and sulphite pulps under laboratory conditions (Fagersham 2004; Fischer and Messner 1992; Gibson 1991; Matsukura et al. 1990; Zhang et al. 2005). Consequently, experiments were conducted to ascertain if these and other enzymes could be effective in further lowering of lipophilic extractives in sulphite pulps. The experiments were conducted on a laboratory scale and in a mill trial.

Pulp Fractionation

Many years ago when sulphite mills were the norm, sulphite pulp was

fractionated to remove fines, which were then disposed of because they contain extractives that cause pitch problems (Dahm and Dannerig 1967; Croon and Ponton 1969). However, studies showed that more than 90% of these fines could be recovered by flotation (Enke 1969). For example, after a separate alkaline treatment, fines from European spruce and hardwood sulfite pulps were rendered fairly harmless and could be recycled to the bulk of the pulp in the alkaline extraction stage of bleaching. No separate washing or thickening of the fines was then necessary, and the surplus alkali was available for use (Enke 1969). Also, for pine sulphite pulps, separate treatment of fines showed no advantage over alkaline treatment of the whole pulp. This technology of fibre fractionation was revisited to assess if it would be applicable to Canadian sulphite pulps.

EXPERIMENTAL

Alkaline Washing

Unbleached ammonium sulphite pulp samples were subjected to simulated single stage washing by using 2% alkaline solution in a Buchner funnel. Different amounts of alkaline were used to reach to a final pH between 6 and 10.5.

Enzyme Treatment

First laboratory evaluations

An unbleached pulp sample from an ammonium sulphite pulp mill (before oxygen delignification) was treated with a lipase enzyme and then bleached. The chemistry of its lipophilic extractives was studied and compared to those of a pulp sample that had very low lipophilic extractives (alpha pulp). Lipase treatment of pulp having 10% consistency was carried out at 40 °C and pH 6 for three hours. Following enzyme treatment, the pulp was bleached with ClO₂ at 3.5% consistency for 50 minutes.

Second laboratory evaluations

Another laboratory trial was conducted to assess the efficacy of using laccase and lipase enzymes in reducing the extractives content of pulps. Previous research has shown that resin and fatty acids are susceptible to oxidation by laccase (Zhang et al. 2005). Since previous studies have shown that glycerides are present in final bleached sulphite pulps, it was considered prudent to investigate treatment of the fully bleached pulp with lipase enzymes to assess if the treatment could further reduce the extractives in the pulp.

Conditions

Brown stock samples were collected after the post extraction washer (PEW), before oxygen delignification. The laccase used in this study was a *Trametes versicolor* laccase supplied by Wacker Chemie (Munich, Germany). Laccase treatments were carried out under conditions specified below. The control experiments were run under identical conditions without the addition of enzymes.

- Laccase enzyme treatment:
 - Retention time 2 hours
 - Temperature 50°C
 - pH 5.0
 - Consistency 10%

A fully bleached final pulp was treated with lipase.

- Lipase enzyme treatment
 - Retention time 3 hours
 - Temperature 40°C
 - pH 6.0
 - Consistency 10%

The lipophilic extractives of the pulps were determined before and after enzyme treatments, and their components were determined by GC.

Mill Evaluation

From the results of the laboratory trials, a commercial lipase enzyme formulation was procured for a mill trial.

The potential activity of the enzyme under mill conditions was evaluated initially by ascertaining the effects of pH and temperature on its activity in the laboratory. The lipase enzyme, Buzyme 2528 (Buckman Laboratories) was dosed on pulp at 0.5 kg/t for 1 hour under varying pH (4-10) and temperature (70 – 90°C) conditions. The pulp consistency was adjusted to 3.5% to enable mixing in the laboratory.

A mill trial was conducted using the optimum conditions determined from the preceding study. The enzyme formulation was diluted from 600 L to 1090 L with mill water, resulting in a 55% concentrate. It was then dosed at 1.6 kg/t (prior to the O₂ tower) for a 3-day trial period. Samples were collected in time-line sequence, prior to the trial, during the trial, and after the trial at the following unit operations: chemi-washer (prior to enzyme addition), post-extraction washer (after enzyme addition point), and the final pulp. The mill was using fresh chips (60% black spruce: 40% eastern white pine) at the time.

Pulp Fractionation

Two sulphite pulps from the same mill, a high viscosity pulp (grade A) and a low viscosity pulp (grade B), were fractionated using a Bauer-McNett fractionator. 14-, 28-, 48-, 100-, and 200-mesh screens were used: these corresponded to sieve openings of 1.19, 0.595, 0.297, 0.149, and 0.074 mm, respectively. The fraction retained by the 14-mesh screen is called R-14, by the 28-mesh screen, R-28, etc. The fraction that passed through all the screens, or P-200, is also defined as the fines fraction. Usually, the P-200 fraction is not retained and its amount is determined by a mass balance. For our purpose, the P-200 fines fraction was retained by passing it through a 450-mesh screen (sieve opening of 0.029 mm), and will thus be called R-450. More details on the fractionation steps can be found in the literature, for example, Gooding and Olson (2001).

Analysis of Extractives in Pulps

The pulp samples were freeze-dried, ground to ensure homogeneity, and then extracted with acetone or dichloromethane. Details of the extraction procedure have been previously described (Sithole et al. 1991). The extracts were processed as shown in the schematic in Fig. 1.

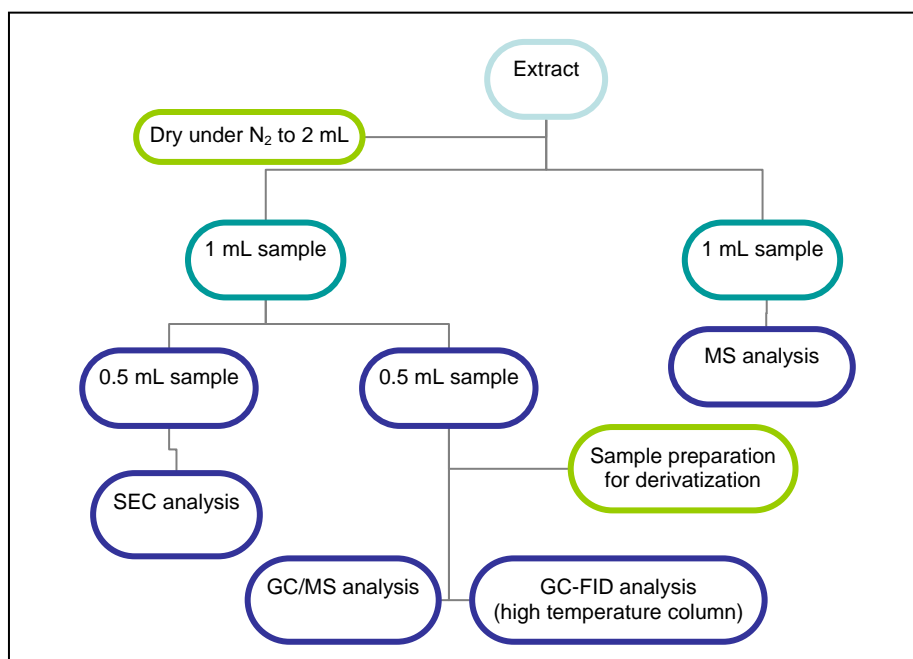


Figure 1. Manipulation of lipophilic extracts of pulps

Derivatization

The extractives were dried and reconstituted in 1 mL MeOH-MTBE (1:9) in a GC vial. Nitrogen was bubbled to a solution mixture made of 8.0 mL diethyl ether, 4.0 mL ethoxyethanol, 0.4 g Diazald® (Aldrich Chemical Company, Inc.), and 4.0 mL 11 N KOH. The diazomethane produced was then redirected and bubbled into the GC vial containing the extracts. The sample was dried under nitrogen and reconstituted in 0.5 mL of methanol.

Instrument Conditions

GC-FID

GC: Hewlett Packard 5890 Series II

Column: DB5-HT, 30 m x 0.32 mm x 0.10 µm capillary column

Carrier: Helium, 29.9 cm/s

Oven: 100 °C (5 min) to 200 °C at 10 °C/min, 200 °C (3 min) to 245 °C at 2 °C/min, 245 °C to 360 °C at 10 C/min., 360 °C (22 min)

Injector: 360 °C, Split 25:1

Detector: FID, 370 °C

Data processing: HP ChemStation, Rev. A.06.01

Details on characterization and analysis of wood resin components have been previously described (Sitholé et al. 1992)

Size Exclusion Chromatography (SEC)

The extracts were dissolved in tetrahydrofuran (~1400 ppm), filtered through 0.45 µm PTFE membrane filters, and then characterized by SEC. A 50-µL volume of the sample was injected and eluted at a flow rate of 0.7 mL/min (Waters 515 pump). Three Shodex columns (KF series with exclusion limits of 107, 106, and 105, respectively) were connected in series for fractionating the samples. Tetrahydrofuran was used as an eluent. The eluting compounds were detected using a UV detector (Waters 486) set at 254 nm wavelength. Polystyrene was used for calibrating the molecular weight distributions.

RESULTS AND DISCUSSIONS

Alkaline Washing

The results showed that more lipophilic extractives were removed at higher pH values than at the lower ones. The following relations were ascertained:

$$E = -0.019 \text{ pH} + 0.492$$

$$R = 5.1653 \text{ pH} - 30.847$$

$$(E = \text{DCM extractives, \%}; \quad R = \text{Removal of extractives, \%})$$

These results were encouraging enough that a mill trial was conducted in the hope that higher pH at the third washer would improve the removal of lipophilic extractives from the sulphite pulps. The results are shown in Table 1.

Table 1. Effect of pH at Washer Vat on Residual Lipophilic Extractives

pH at Third Washer Vat	DCM Extractives, %
11.2	0.103
11.	0.073
12.3	0.033
11.2	0.113
11.2	0.103
11.2	0.124
11.2	0.114

It appears that strong alkaline conditions in the extraction tower may have been the dominating factor affecting the removal of lipophilic extractives. Thus increasing pH beyond 11.2 was beneficial in terms of removal of lipophilic matter. However, this comes at a high cost because caustic is expensive and affects cellulose chain length, as indicated by lower viscosity of the pulps (Lapierre et al. 2006).

Enzyme Treatment

First laboratory studies

The potential of using lipase treatment to hydrolyze triglyceride in brown stock pulp was first examined. Figure 2 shows the fatty acid and glyceride contents of the samples. It can be seen that there was a decrease in glyceride levels and an increase in fatty acid content with the enzyme treatment. This is expected, since the breakdown of glycerides results in the formation of fatty acids and glycerol. The glycerol gets washed out from the pulps, whereas the fatty acids remain with the pulp, adding to the fatty acids originally present in the pulp. Overall, there was a 30% decrease in extractives content of lipase-treated pulp versus the control.

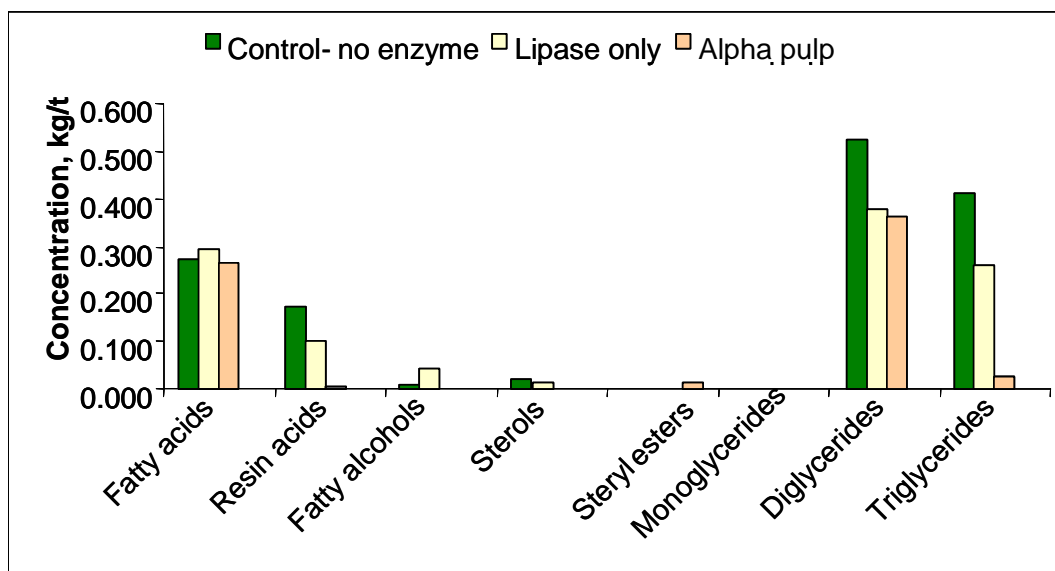


Figure 2. Distribution profile of lipophilic components in pulp extractives

In addition, the results show that enzyme treatment reduced the amount of lipophilic extractives, but not to the extent achieved in the production of the high purity target pulp. The enzyme treated pulps still had significant amounts of fatty acids, resin acids, and glycerides. It is interesting to note that the major extractable components in the target alpha pulp were fatty acids and diglycerides.

A different bleaching sequence was tried: OEXCDEP instead of OEXDED. In addition, the effect of lipase dosage was also determined. The results are shown in Fig. 3. The relatively high value of the extractives content of the pulp was probably due to recirculation of the wash water laden with extractives at the mill.

This bleaching sequence reduced the extractives content by almost half when compared to the control sample. Although it is evident that there was a decrease in the extractives contents with increase in the dosage of the lipase enzyme, the decrease was not proportional to the dosage. In reality the decrease was minimal, considering that one dosage is 2.5 times the other one. The profile of the individual components present in the extracts is shown in Fig. 4. The profile indicates that the components were reduced by

almost half in the enzyme-treated samples, versus the untreated control sample. Unlike in the previous bleaching sequence, the amounts of fatty acids had decreased and not increased as seen before. This is because the introduction of the Ep stage facilitates removal of fatty acids, owing to the alkaline conditions.

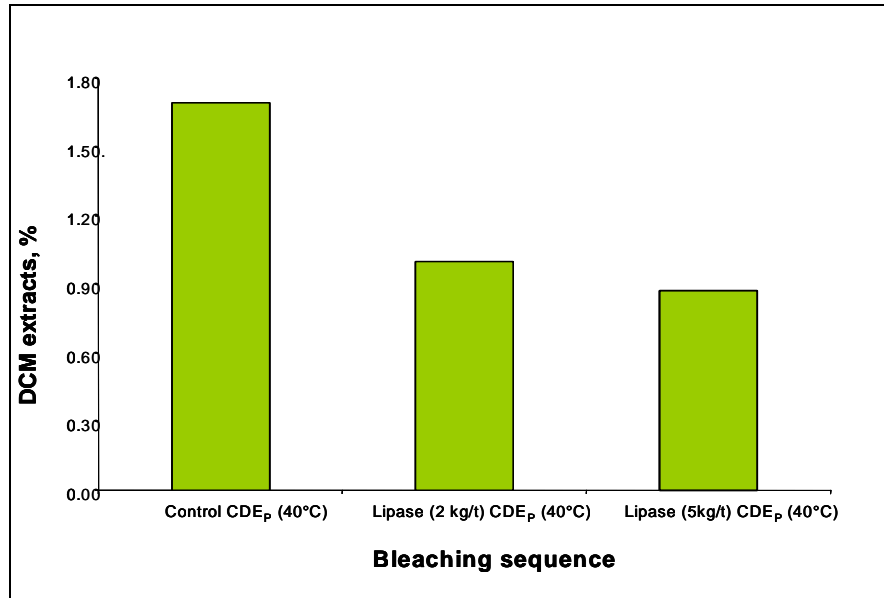


Figure 3. Effect of enzyme treatment and different bleaching sequence on the extractives contents of a sulphite pulp

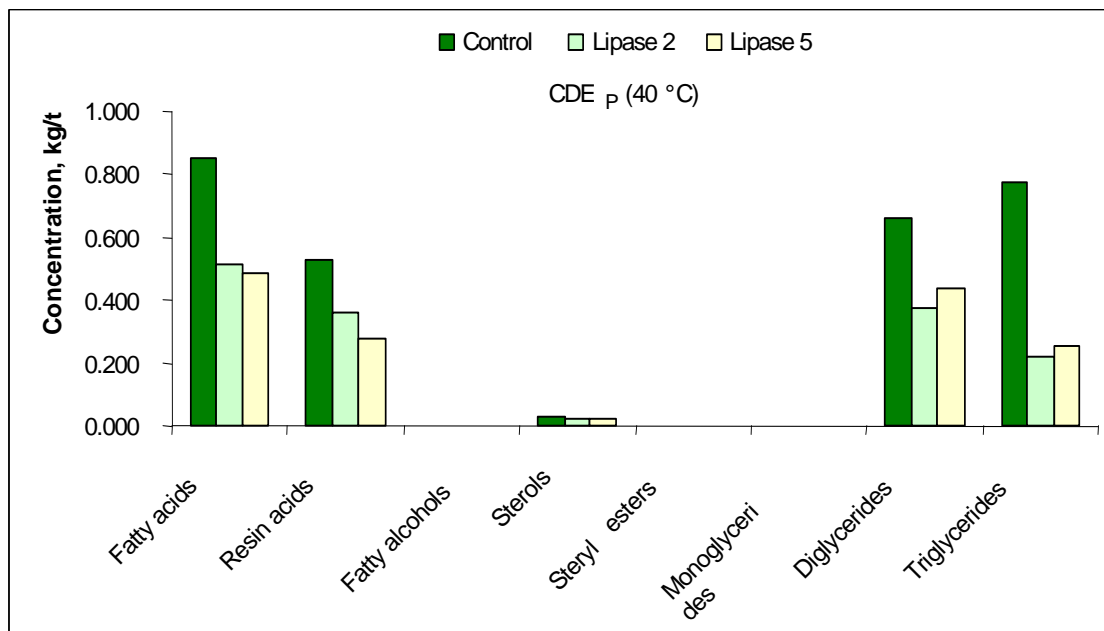


Figure 4. Distribution profiles of the individual components present in the pulp extractives

Second laboratory studies

Results from GC analysis of the extractives components of the original untreated pulps are shown in Figs. 5 and 6. It is evident that there were considerable amounts of resin and fatty acids (retention times between 3-10 minutes), lignans and sterols (retention times between 10-15 minutes), and esters (retention times between 15–28 minutes) in the PEW pulp. The ester group includes both steryl esters and triglycerides (Fig. 5).

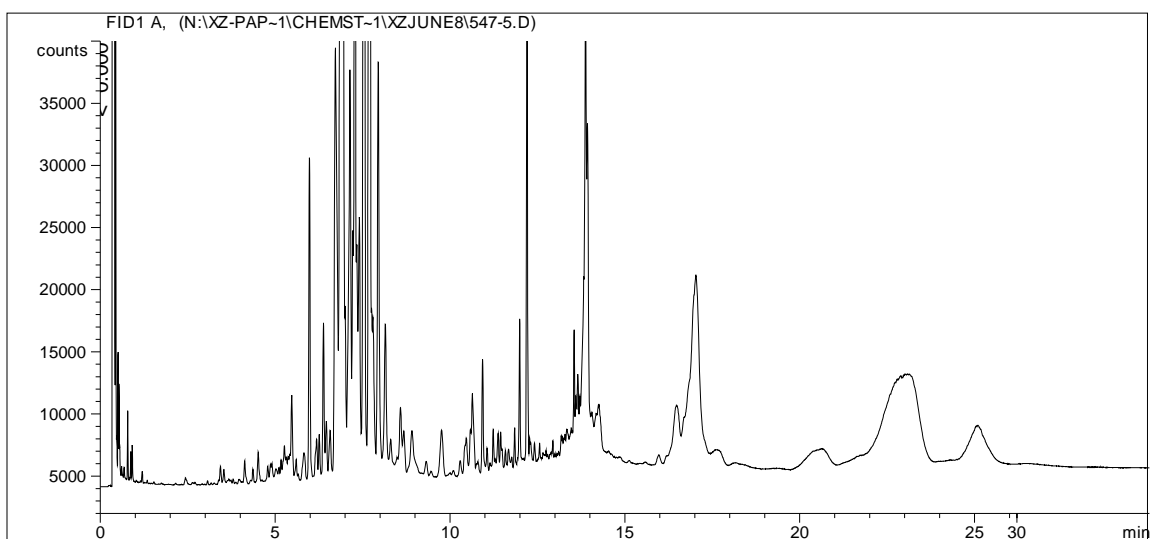


Figure 5. GC chromatogram of extractives of PEW pulp (Total extractives were $2.41 \pm 0.02\%$. Retention time: 3-10 minutes: resin and fatty acids; 10-15 minutes: lignans & sterols; 15-28 minutes: steryl esters & triglycerides)

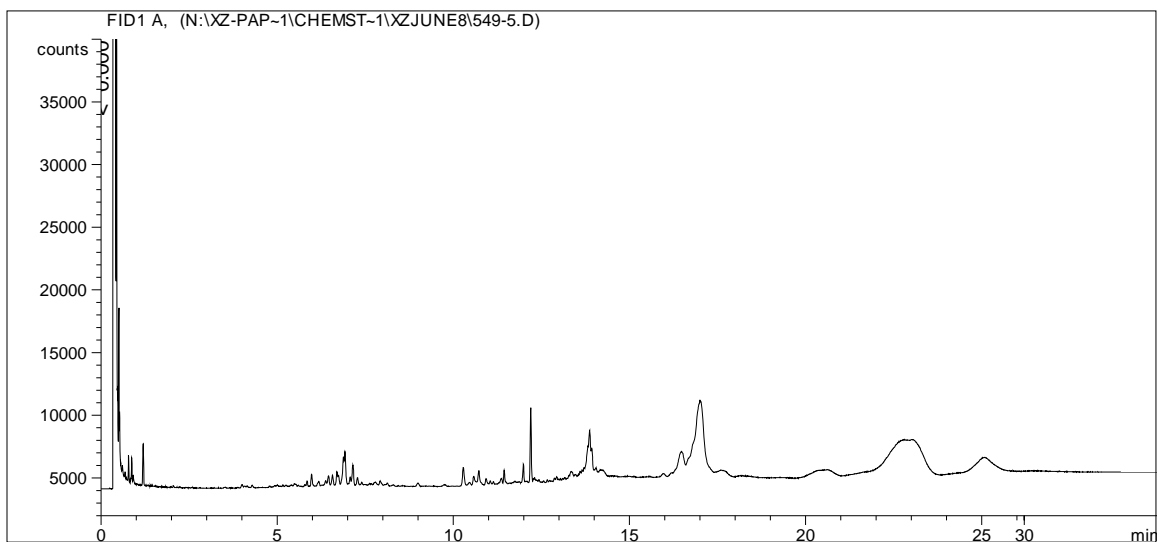


Figure 6. GC chromatogram of extractives of final pulp (Total extractives were $0.393 \pm 0.03\%$. Retention time: 3-10 minutes: resin and fatty acids; 10-15 minutes: lignans & sterols; 15-28 minutes: steryl esters & triglycerides)

Most of these extractives were degraded through the subsequent bleaching process with little remaining in the final pulp (extractives decreased from 2.41% to 0.393%). As shown in Fig. 6, the residual extractives consisted mainly of esters (peaks between 15-28 minutes) and probably some sterols (peaks between 10-15 minutes).

Results for enzyme treatment of the pulp with oxidative enzymes are shown in Tables 2 to 4. Laccase treatment of unbleached sulphite pulp resulted in little removal in total extractives content of the pulp after 2 hours of enzymatic treatment (Table 2).

Table 2. Extractives Contents Present in PEW Pulp and Laccase Treated PEW Pulp

Sample	Percentage of extractives in pulp (%±sd)
Original PEW pulp	2.41 ± 0.02
Control PEW pulp (after pH adjustment)	2.03 ± 0.01
Laccase at 5 U/g	1.99 ± 0.02
Laccase at 25 U/g	1.96 ± 0.001

Results for treatment with lipoxygenase are shown in Table 3. It should be noted that pH adjustment of the pulp before enzyme treatment resulted in a 45% reduction in lipophilic extractives content of the pulp. This is attributed to alkaline hydrolysis of the glycerides. Treatment with the enzyme resulted in an 8% further removal in the extractives content of the pulp. Treatment with enzyme for 2 hours at 30°C gave a further decrease in extractives content. GC analysis of the components in the extractives showed that the removal caused by lipoxygenase was due mainly to the degradation of fatty acids.

Table 3. Extractives Contents Present in PEW pulp and Lipoxygenase Treated PEW Pulp

Sample	Percentage of extractives in pulp (%±sd)
Original PEW pulp	2.41 ± 0.02
Control PEW after pH adjusted to 9	1.36 ± 0.06
Lipoxygenase at 1mg/g (pH 9)	1.25 ± 0.012
Lipoxygenase at 7.5mg/g (pH 9)	1.26 ± 0.004

The laccase and lipoxygenase enzymes were also tested on the final pulp. However, no significant removal in extractives content was detected after 2 hours of treatment. This was not unexpected, considering that glycerides were the major components in the extractives of the final pulp (as can be seen in Fig. 6). Results for lipase treatments of the final pulp are shown in Table 4. It was found that the lipase treatments did not significantly change the total extractives content. However, GC analysis of the extracts showed that both lipases hydrolysed the triglycerides (peaks between 20 to 25 minutes) and converted them into fatty acids (Fig. 7 compared to Fig. 6). The rest of the extractives (other peaks) remained unchanged. Previous work has shown that most fatty and resin acids are susceptible to breakdown during oxidative bleaching, while esters are more tolerant to bleaching sequences. It is conceivable that a more effective reduction of extractives content in the pulps can be obtained if the lipase enzyme treatment is performed before the bleaching process. This way, most of the esters can be hydrolyzed to fatty acids by lipase pretreatment and then be degraded by the

subsequent bleaching. This approach was recommended for a mill trial.

It is worth noting that most of the steryl esters (at 17 minutes) are not removed by lipase treatment. Consequently, finding an effective esterase enzyme targeting these compounds would likely help to further reduce residual extractives in sulphite pulps.

Table 4. Extractives Contents Present in Final Pulp and Lipase Treated Final Pulp

Sample	Percentage of extractives in pulp (%±SD)
Original final pulp	0.39 ± 0.03
Control at pH 5	0.35 ± 0.03
Lipase 1 (5 mg/g)	0.34 ± 0.04
Lipase 2 (5 mg/g)	0.33 ± 0.01

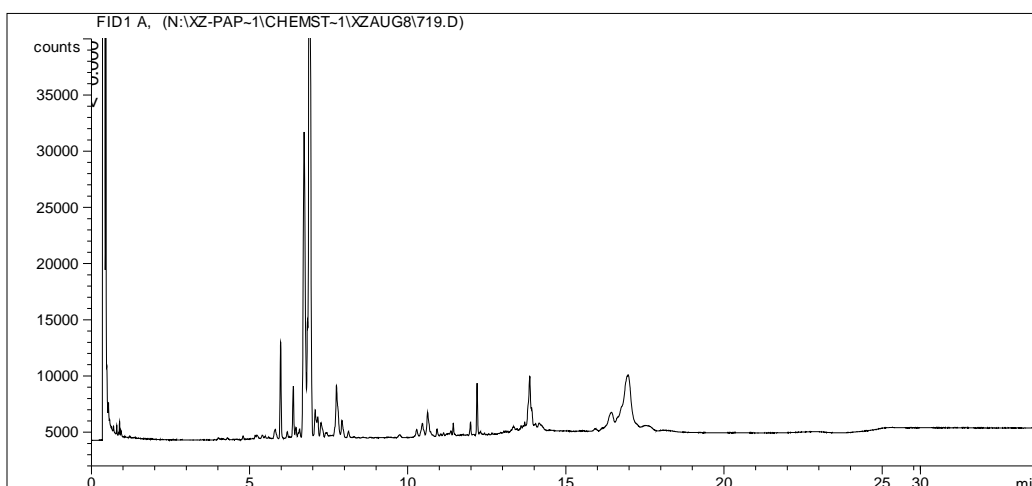


Figure 7. The residual extractives present in final pulp after lipase treatment (note conversion of triglycerides to fatty acids). Retention time: 3-10 minutes: resin and fatty acids; 10-15 minutes: lignans and sterols; 15-28 minutes: steryl esters and triglycerides.

Mill Trial

The results shown in Fig. 8 indicate that the activity of the enzyme breaks down at high temperatures and pH. The optimum conditions for the enzyme appear to have been 70 °C at pH 6-8.

The amounts of lipophilic extracts in the pulp samples are shown in Table 5. The data show the following:

- In the chemi-washer (CW) samples, the control and enzyme-treated pulps contained the same amount of extractives. The amounts of extractives here correspond to about 50% of the extracts that were in the starting chips. This is a consequence of the acid conditions that are not conducive to efficient removal of wood resin compounds. (The chemi-washer is located right after the red stock.)
- Results for the post-extraction samples show a dramatic difference between the

control and enzyme-treated samples. Enzyme treatment resulted in a 50% removal of extractives versus the control sample (0.12 vs. 0.06%).

- The removal was reflected in the final pulp but was not as dramatic (17% removal). This is probably a reflection of the mill's process, where there is recirculation of some of the wash water.

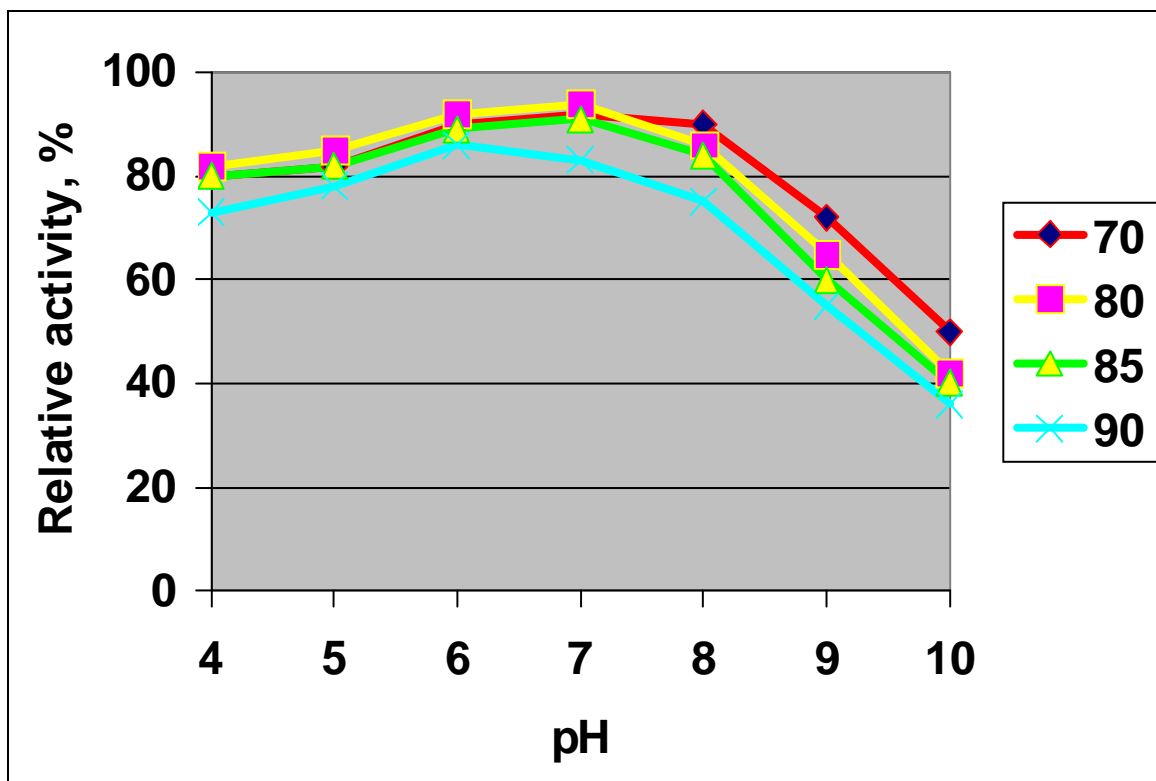


Figure 8. Effect of temperature and pH on the activity of a commercial lipase enzyme

Table 5. Results for a Mill Trial with a Commercial Lipase Enzyme

Sample	Unit operation and amount of extractives in pulp (%)		
	Chemi-washer	Post-extraction washer	Final pulp
Control (pre-trial)	1.65	0.12	0.030
Trial	1.64	0.06	0.025
Control (after trial)	1.83	0.11	0.028

To better assess the conversion and composition of the components in the extractives, the extracts were further analyzed by GC-FID. The results are shown in Table 6.

Table 6. Extractives Composition and their Concentration (expressed as percentage of pulp) from GC-FID Analysis

Sample	Fatty alcohols	Fatty acids	Glycerides	Resin acids	Sterols	Steryl esters	Total
CW control	0.004	0.2606	0.1230	0.1820	0.0233	0.015	0.6079
CW trial	0.004	0.2608	0.1229	0.1816	0.0230	0.015	0.6073
PEW control	0.0002	0.0042	0.0085	0.0035	0.0038	0.0017	0.0212
PEW trial	0.0002	0.0013	0.0051	0.0021	0.0013	0.0006	0.0107
Final control	0.0009	0.0019	0.0117	0.0006	0.0015	0.0009	0.0175
Final trial	0.0008	0.0013	0.0093	0.0005	0.0007	0.0006	0.0133

The data show that glycerides accounted for 0.12% of the lipophilic extracts in the chemi-washer pulp whereas they were the predominant components present in the PEW and final pulp extractives, in both the control and trial samples. In the PEW pulps, there was a 40% drop in glycerides content in the enzyme treated pulp compared to the control pulp. A 20% drop in glycerides content was observed in enzyme treated final pulp when compared to the control pulp. If the enzyme degradation of glycerides is efficient and converts all of the glycerides to fatty acids and glycerol, then the best possible removal of the extractives would result in residual extractives of 0.0040% in the final pulp. However, in reality the residual extractives in the final pulp during the trial were 3 times higher at 0.0133%. Thus it appears that enzyme treatment did not completely break down the glycerides. The fatty acids formed during enzymatic degradation of the glycerides are mostly removed as soaps during the alkaline wash stages.

Pulp Fractionation

Tables 7 and 8 summarize the fibre distribution results obtained for the two grades of sulphite pulps. The distributions, quite similar, are dominated by the R-14 fraction with progressively smaller amounts of the shorter fibre fractions.

Table 7. Results for High Viscosity Pulp (Grade A)

	Whole pulp	Fraction					
		R-14	R-28	R-48	R-100	R-200	R-450
% Weight	-	39.1	33.1	13.9	7.1	3.1	3.7
St. Dev.	-	1.5	1.1	0.5	0.3	0.4	0.1
Extractives (%)	0.144	0.077					1.88

Table 8. Results for Low Viscosity Pulp (Grade B)

	Whole pulp	Fraction					
		R-14	R-28	R-48	R-100	R-200	R-450
% Weight	-	35.4	28.2	14.6	10.6	5.6	5.5
St. Dev.	-	1.8	1.0	0.4	0.1	0.1	0.2
Extractives (%)	0.123	0.073					0.98

For the high viscosity pulp, the ratio of the extractive contents of the pulp free of fines (0.077%) over the pulp with fines (0.144%) was 0.53. For the low viscosity pulp, the equivalent ratio was $0.073 / 0.123 = 0.59$. Therefore, removing the R-450 fraction in either pulp will result in a decrease in the residual lipophilic extractives by almost a factor of one half. The amounts of lipophilic extractives in the R-450 fractions, calculated by a mass balance, were 1.88% for Grade A and 0.98% for Grade B. The ratio of lipophilic extractives found in the fines fraction over the entire pulp was 13.1 for Grade A and 8.0 for Grade B.

As the results were very encouraging, it was decided to ascertain if the process could be beneficial, on a larger scale, for a pulp with very low lipophilic extractives. Accordingly, 100 kg (oven dried) of alpha pulp was fractionated in Paprican's fractionation pilot plant. The pulp was soaked for 72 hours at 0.927% consistency. Analysis by a Fibre Quality Analyzer (FQA) indicated that it contained approximately 8% fines material (defined to be between 0.07 and 0.2 mm). The pulp was heated to 60°C and passed through a screen (0.04 inch holes). The accepts obtained from this screening stage contained 24% fines (as per FQA) at a consistency of 0.28%. The rejects (long fraction) were at a consistency of 2.74%. After heating back up to 60°C, the short fraction was then passed through a set of hydro cyclones, and the accepts had approximately 45% fines (FQA analysis) at a consistency of 0.06%. The rejects were combined with the previous rejects, and the combined long fractions were at a consistency of 1.26%. The results, summarized in Table 9, confirm previous observations that the short fibres are associated with much more lipophilic extractives than the long ones. This is because the short fibres have higher surface area (on which the extractives are adsorbed) than long fibres and have higher levels of parenchyma cells that contain wood resin.

Table 9. Average Values of DCM Extractives in Pulp (%±sd)

	Whole pulp	Long fraction	Short fraction
Extractives, %	0.030 ± 0.005	0.020 ± 0.003	0.050 ± 0.003

The data indicate that fractionation of this pulp will reduce the residual lipophilic extractives from 0.030% to 0.020%, which is quite a significant removal.

To better assess the composition of extractives in the different fractions, the extractives were further analyzed by GC, SEC, and mass spectrometry.

GC-FID

Based on the chromatographic separation, the individual compounds can be grouped into their corresponding families as illustrated in Figure 9.

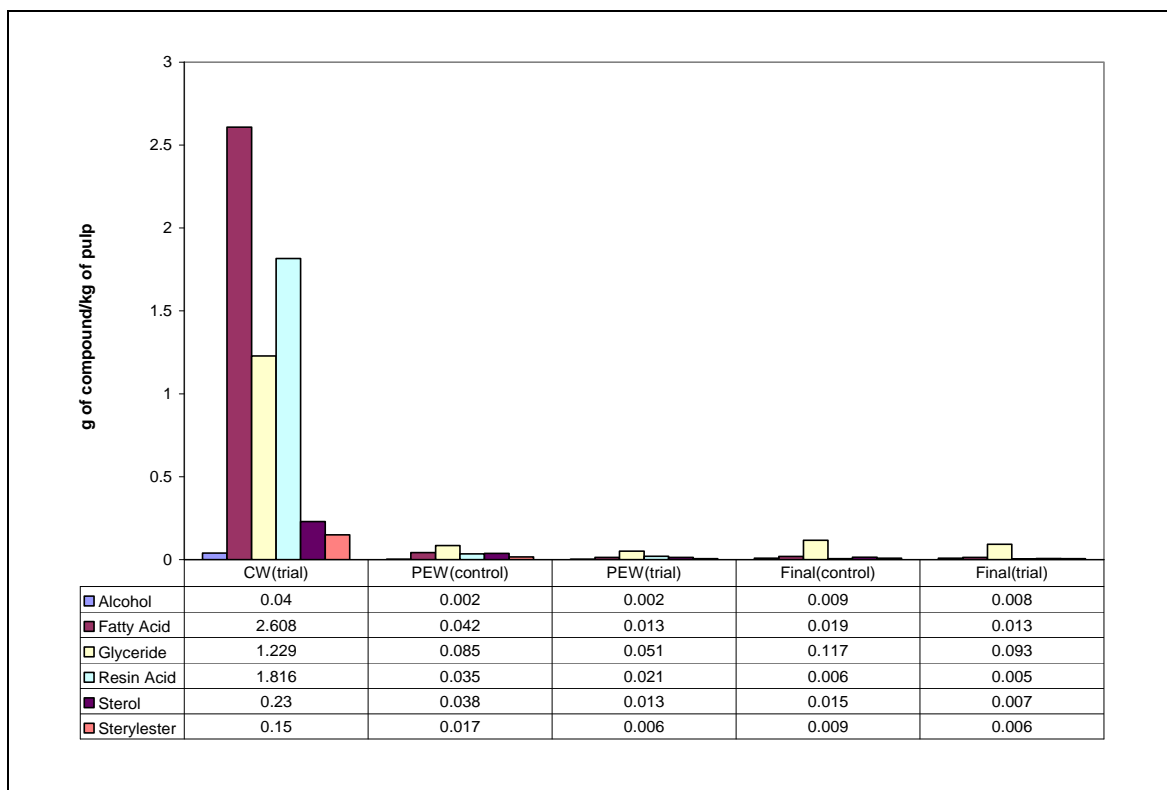


Figure 9. Distribution of organic compounds in various pulp fractions

It is evident that the short fractions were associated with much higher amounts of lipophilic extractives components than the long fractions. In addition, the short fractions contained much larger amounts of glycerides, sterols, and steryl esters than the long fractions. These data explain why removal of the fines fraction would result in a significant removal in the extractives content of the final pulp.

For GC-FID analysis, mass balance calculations showed that the eluted components accounted for only 30, 36, and 31% of the extracts analysed from the original, long, and short fractions, respectively. As previously mentioned, this is due to the presence of high molecular weight compounds in the extracts that are not amenable to analysis by gas chromatographic techniques.

Another apparent feature in the chromatography of the extracts was the presence of higher amounts of low molecular weight compounds in the short fractions than in the long fractions. The peaks are attributed to short chain fatty acids and alcohols (less than C₁₆). The higher surface area of the fines probably explains this observation.

Size Exclusion Chromatography

SEC is a technique that separates compounds according to molecular size. Low molecular weight compounds elute last, as they have to enter the interstices of the column matrix and thus take a long time to elute. High molecular weight compounds are too big to enter the interstices and thus are eluted much more quickly than the low molecular weight ones.

Molecular weight distributions of the extractives from the various fractions are shown in Fig. 10 in the form of relative concentration versus elution volume. From this plot the following observations can be made:

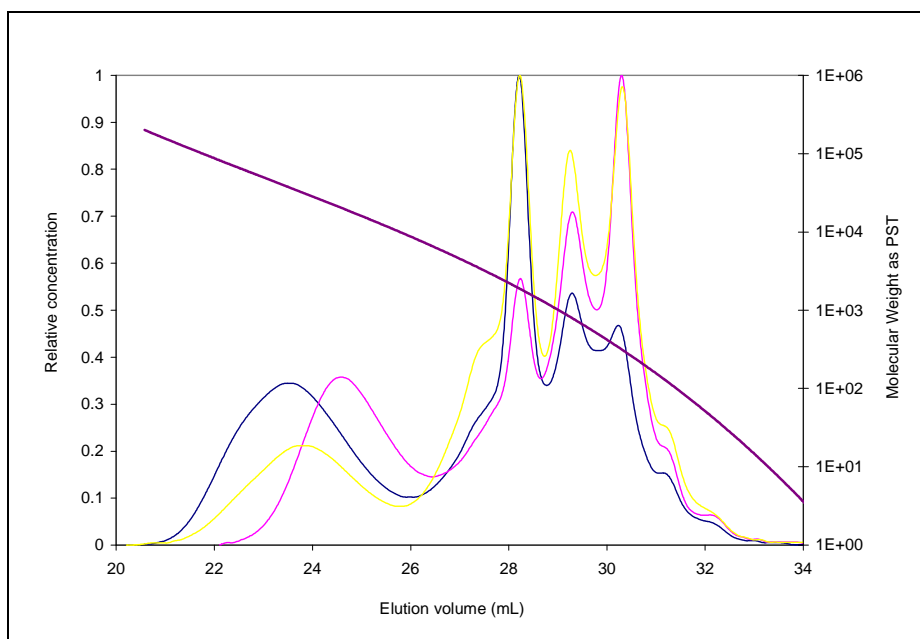


Figure 10. Size exclusion chromatograms of lipophilic extracts of fibre fractions
 ---Whole pulp ---Long fraction ---Short fraction --- Polystyrene standard (PST)

- The three pulp fractions contained the same type of low molecular weight compounds, as evidenced by the similar elution profiles in the 28-34 mL elution volumes.
- There were differences in the high molecular weight components present as seen in the 20-28 mL elution volumes: the whole pulp contained components that were of higher molecular weight than both the short and long fractions. The molecular weights of components in the short fraction lay in between those of the whole and long fraction. The molecular weights of these fractions were in excess of 1000, which is indicative of polymerized fatty acid and glyceride-type compounds. It appears that the highest molecular weight components were associated with the short fraction.

Mass Spectrometry

Analysis of the three fractions by mass spectrometry showed that major components were distributed between m/z 149 to m/z 1022. Due to the limitations of the experimental conditions used, it was hard to obtain structural data on the high molecular weight compounds. However, a few peaks were observed around 1600 to 1900 m/z in the long fibre fraction at very low intensity. These m/z values are indicative of polymerized wood resin. When MS/MS collision studies were performed on the 741, 1022, and 1398 m/z fragments, ESI-MS and MS analysis showed that most of these peaks originated from glycerides (mainly mono- and di-) and steryl esters.

CONCLUSIONS

Alkaline Washing

It appears that strong alkaline conditions in the caustic extraction tower may be the dominating factor affecting the removal of lipophilic extractives. Thus increasing pH beyond 11.2 is beneficial in terms of removal of lipophilic matter. However, this comes at a high cost, because caustic is expensive and affects cellulose chain length, as indicated by lower viscosity of the pulps. Thus this is not a viable option for pulps destined for customers that are sensitive to changes in viscosity.

Enzyme Treatment

In laboratory studies, lipase treatments (without washing) did not reduce total extractives content of the final pulp, but were able to convert triglycerides to fatty acids. Lipase treatment with pulp washing reduced the extractives content of the pulp by almost 30%. The final pulp produced during a mill trial of a lipase enzyme treatment showed that there was a 20% decrease in lipophilic extractives content of the pulp relative to a control sample. It is recommended that lipase treatment prior to the bleaching sequence would lead to better removal of extractives in the pulp. However, unlike in the laboratory studies, the major components in the extracts were glycerides. This indicates that the enzyme did not completely degrade the glycerides under the mill conditions used. Finding an enzyme that can effectively degrade the residual steryl esters will provide a key solution to reduce the amount of extractives in final sulphite pulps. Efforts are currently under way on screening enzymes that may have the potential to do this on sulphite pulp substrates.

Fibre Fractionation

The fines fractions contained 8 to 13 times more residual lipophilic extractives than the whole pulps. Removing this fraction, which represents only a small percentage of the whole pulp, could still reduce by about half the amount of lipophilic extractives in the remaining pulp. Thus, pulp fractionation appears to be a viable option to achieve further deresination of sulphite pulps. It may perhaps be beneficial to subsequently deresinate the fines fraction by treating them with caustic or lipase enzymes. That way, the treatment will be more focused on the more problematic fraction of the pulps. Alternatively, the fines fraction could be used elsewhere where wood resin content is not

a major issue, e.g., as a filler in the middle layers of ply board products.

From the results of these studies, it is apparent that there is still a need for more research into methods for deresination of sulphite pulps. Methods such as removal of wood resin by flotation and/or centrifugation will be explored. A Paprican patent on removal of wood resin from process streams by centrifugation showed that the technology enabled 35% deresination of the streams in a kraft mill (Allen and Lapointe 1996). It would be interesting to ascertain if the technology is also applicable to sulphite pulp mills. In addition, it is desirable to find effective environmentally friendly surfactants for deresination of sulphite pulps. Surfactants currently used as replacement for nonyl phenol ethoxylates are, apparently, not as effective as the NPEs in deresination of sulphite pulps.

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LITERATURE CITED

- Allen, L. H., and Lapointe, C. L. (1995). "Centrifugal removal of extractives for system closure," *U.S. Patent* No. 5468396, issued November 21, 1995.
- Back, E., and Allen, L. H. (2000). *Pitch Control, Wood Resin and Deresination*, E. L. Back and L. H. Allen (eds.), TAPPI Press, 307-328.
- Croon, I., and Ponton, S. (1969). "Aids for pitch control in pulp mills," *Svensk Papperstid.* 72(16), 498-508.
- Dahm, H. P., and Dannevig, Jr., E. (1967). "Recovery and use of fines from fiber fractionation," *Norsk Skogind.* 21(11), 432-436.
- Ekman, R. and Holmbom, B. (2000). "The chemistry of wood resin". In: *Pitch Control, Wood Resin and Deresination* (Eds.: E. Back and L.H. Allen), TAPPI PRESS, Atlanta, pp. 37-76.
- Enke, M. (1969). "Experiments aimed at concentration of spruce sulfite fines and subsequent recovery of extractives," *Zellstoff Papier* 18(10), 293-296.
- Environment Canada (2006). "Assessment Report - Nonylphenol and its ethoxylates," <http://www.ec.gc.ca/substances/ese/eng/psap/final/npe.cfm>, (Last updated: 2006-03-10).
- Guenther, K., Heinke, V., Thiele, B., Kleist, E., Prast, H., and Raecker, T. (2002). "Endocrine disrupting nonylphenols are ubiquitous in food," *Environ. Sci. Technol.* 36(8), 1676-1680.
- Health Canada (2006). "Priority substances list assessment report for nonylphenol and its ethoxylates," http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/psl2-lsp2/nonylphenol/nonylphenol_4_e.html, (Last Updated: 2006-02-07).
- Fagerstrom, R. (2004). "Lipases for solving pitch problems in paper," *Ind. Bioprocess* 26(2), 10.

- Fischer, K., and Messner, K. (1992). "Biological pitch reduction of sulfite pulp on pilot scale," Proceedings, 5th International Conference on Biotechnology in the Pulp and Paper Industry, Japan TAPPI, Uni Publishers Co. Ltd., Tokyo, p. 169-174.
- Gibson, K. (1991). "Applications of lipase enzymes in mechanical pulp production," Proceedings, TAPPI Pulping Conf., TAPPI Press, Atlanta, Book 2, p. 775-780.
- Gooding, R. W., and Olson, J.A. (2001). "Fractionation in a Bauer-McNett Classifier," *J. Pulp Pap. Sci.* 27(12), 423-428; http://www.api.ubc.ca/people/olson/01-12-05_OlsonGooding_JPPS_Bauer.pdf
- Lapierre, L., Bouchard, J., and Berry, R.(2006). "On the relationship between fibre length cellulose chain length and pulp viscosity of a softwood sulfite pulp", *Holzforschung* 60(4): 372-377.
- Matsukura, I. Y., Usui, M., and Hata, K. (1990). "Enzymatic pitch control in papermaking system," Proceedings, TAPPI Papermakers Conf., TAPPI Press, Atlanta, p. 1-10.
- Mouyal, P. (2005). "Efficient resin removal," *Paper Age*, Nov/Dec., 34-35.
- Sitholé, B. B., Vollstaedt, P., and Allen, L. H. (1991). "Comparison of Soxtec versus Soxhlet systems for the determination of wood extractives (lipids)," *TAPPI J.* 74(11), 187-191.
- Sitholé, B. B., Sullivan, J. L., and Allen, L. H. (1992). "Identification and quantitation of wood acetone extractives (lipids) by gas chromatography and Lotus 1-2-3," *Holzforschung*, 46(5), 409-416.
- Sithole, B., Shirin, S., and Ambayec, B. (2009). "Analysis and fate of lipophilic extractives in sulphite pulps," in press, *J. Wood Chem. Techn.*
- Zhang, X., Renaud, S., and Paice, M. (2005). "The potential of laccase to remove extractives present in pulp and white water from TMP newsprint mills," *J. Pulp Pap. Sci.* 31(4), 175-180.

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