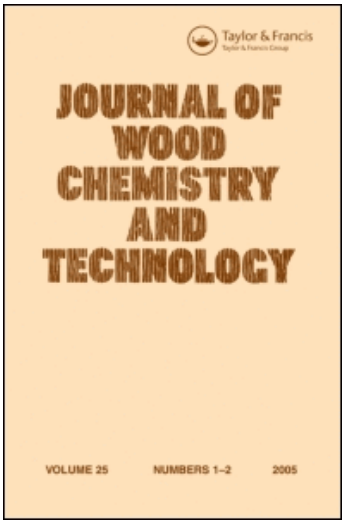

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Analysis and Fate of Lipophilic Extractives in Sulphite Pulps

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Abstract: One of the major requirements of sulphite pulps, particularly those used in the manufacture of dissolving grades, is that their extractives content must not exceed certain levels, as specified by the customer. Since these levels are generally very low, the accuracy and reproducibility of extractives measurements can be poor, which in turn can lead to disagreements between pulp suppliers and their customers. In an effort to improve the reliability of extractives measurements, we have evaluated several methods for the determination of lipophilic extractives in sulphite pulps, using Soxhlet and Soxtec solvent extraction and various modes of drying the extracts including hot plate, infrared lamp, and freeze drying. Analysis of the extracts by size exclusion chromatography showed that a significant portion of the extracts was polymerized during the production process. Lipophilic extractives from ammonium sulphite pulps contain more polymerized matter than the extractives from the magnesium process.

Keywords: analysis, extraction, extractives, lipophilic, pitch, solvents, wood resin

INTRODUCTION

Dissolving pulps are chemical pulps that are suitable for subsequent chemical conversion into such products as rayon, cellophane, cellulose acetate, cellulose nitrate, and carboxymethyl cellulose. They can be manufactured by either a modified kraft or, more commonly, by a sulphite process to produce a relatively pure and uniform cellulose product with a controlled weight-averaged degree of polymerization. Lignin and hemicelluloses are considered

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contaminants and are removed. Lipophilic extractives are another class of contaminants that need to be removed, especially in products destined for the pharmaceutical industry such as carboxymethyl cellulose. 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.[1] Fatty acids, sterols, sterol esters, and glycerides can survive the cooking and bleaching processes and consequently can accumulate in the pulp, adversely affecting the quality of the finished pulp. As well, some of these compounds, which are non-polar in nature, may easily adhere to hydrophobic surfaces of the paper machine and build up pitch deposits. Even small residual amounts of extractives may cause odour and taste problems. Hence, it is important to ensure that sulphite pulps have the lowest amounts of these compounds as possible.

Thus, one way to ascertain the quality of dissolving pulps is to determine their amounts of lipophilic extractives. This is commonly done by measuring their solvent extractives content using standard methods (e.g., TAPPI, SCAN, and PAPTAC).[2] Unfortunately, this is not easy to do due to the low amounts of lipophilic extractives remaining in the pulps; hence there are problems in obtaining good repeatable data. This can cause discrepancies between measurements made by the pulp suppliers and their customers. With this in mind, we set out to study parameters that affect the measurement of lipophilic extractives in sulphite pulps and to determine the best conditions for ensuring accurate and reproducible data. Another objective of this work was to determine the fate of extractives throughout mill operations. Information on the type and level of extractives at different stages of the process could help mills in developing more effective strategies for further reduction of extractives content in their pulps.

A number of papers have been published on the analysis of extractives in wood and pulp matrices. For example, chapters in the book by Back and Allen[3] discuss the effect of solvents of different polarity in extracting wood resin. Also, Bergelin and co-workers[4] evaluated methods for extraction and analysis of wood resin in a chemical pulp. However, their study is applicable to kraft pulps and not to sulphite pulps.

The report is divided into two parts:

1. Determine the best conditions for ensuring accurate and reproducible data in quantifying the amount of lipophilic extractives in sulphite pulps.
2. Determine the fate of extractives throughout mill operations.

PART 1. CONDITIONS FOR ACCURATE AND REPRODUCIBLE DATA

Six different methods were used and evaluated. The methods were based on Soxhlet and Soxtec extractions and various modes of drying the extracts:

Method 1: Soxhlet extraction for 4 hours with 6 siphonings per hour and hot plate drying. The extracts were dried by evaporation of the solvent on a hot plate. This method was in use in the laboratory of one sulphite mill. The norm for extraction times in standard methods is at least six hours.

Method 2: Soxhlet extraction for 8 hours with 6 siphonings per hour and infrared lamp drying. In this case, the extracts were dried by evaporation using an infrared heating lamp. The method is based, essentially, on conditions specified in PAPTAC Standard method G13.[2]

Method 3: Soxhlet extraction for 8 hours with 6 siphonings per hour. After extraction, the extracts were freeze-dried; that is, no heat was used to dry them. That is, the extracts were frozen and then subjected to vacuum to remove the solvent

Method 4: Soxtec extraction for one hour, and drying of extracts on the Soxtec apparatus. Here the solvent was removed using the heater in the extraction unit.

Method 5: Soxtec extraction for one hour, and drying, plus additional drying in an oven at 105°C. After drying the samples on the extraction unit, the extracts were dried further in an oven.

Method 6: Soxtec extraction for one hour, and freeze-drying of extracts. After extraction, the extracts were dried using a freeze-dryer.

In each case, the final dried extracts were conditioned to constant weight in a desiccator. Seven replicates were done for each method.

Soxhlet Extraction

A Soxhlet extractor (see schematic in Figure 1) is a type of laboratory glassware invented in 1879 by Franz von Soxhlet.[5] It was originally designed for the extraction of lipids from a solid test material, but can be used whenever it is difficult to extract any compound from a solid. Typically, dry material is placed inside a filter paper thimble, which is loaded into the Soxhlet extractor. The extractor is attached to a flask containing a solvent and a condenser. The solvent is heated, causing it to evaporate. The hot solvent vapor travels up to the condenser, where it cools and drips down onto the test material. The chamber containing the test material slowly fills with warm solvent until, when it is almost full, it is emptied by siphon action, back down to the flask. This cycle may be repeated as many times as desired. During each cycle, a portion of the lipid dissolves in the solvent. However, once the lipid reaches the solvent heating flask, it stays there. It does not participate in the extraction cycle any further. This is the key advantage of this type of extraction; only clean warm solvent is used to extract the solid in the thimble. This increases the efficiency of the extraction when compared with simply heating up the solid in a flask with the solvent.

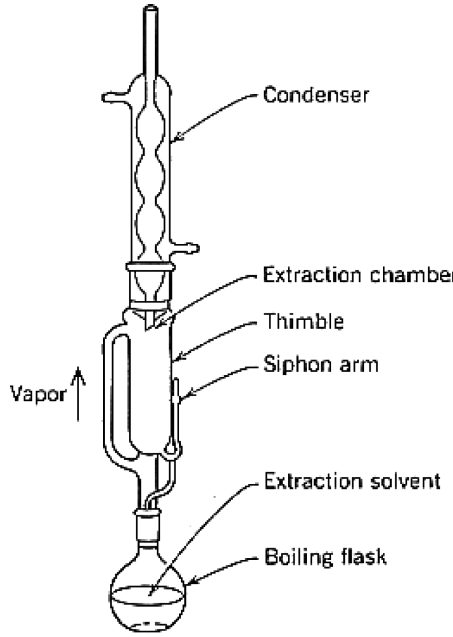

Figure 1. Schematic of a Soxhlet extractor.

At the end of the extraction, the excess solvent may be removed using a rotary evaporator leaving behind only the extracted lipid. In the present study, rotary evaporation was not used, as errors are likely to be high during sample processing, especially for samples with very low lipophilic matter.

Soxhlet extraction was performed on the homogenized samples using acetone as a solvent. About 8 g samples were placed in a cellulose extraction thimble (24.5 mm i.d. × 26.0 mm e.d. × 60 mm length, Whatman™) and extracted with the solvent for 4–8 hours at 6 cycles per hour. The resultant extracts were processed as specified in the methodology being evaluated.

Soxtec Extraction

One century after Soxhlet developed his extraction system, Edward Randall, a chemist from California, designed and patented a unique method, which physically lowered the extraction thimble directly into the flask containing the boiling solvent. Most of the extractable materials readily passed from the sample and dissolved in the organic solvent (similar to a tea bag in hot water). To remove the residual extractable material, it was necessary to raise the sample above the boiling solvent and then drip freshly condensed solvent through it. A schematic of the Soxtec extraction unit is shown in Figure 2.

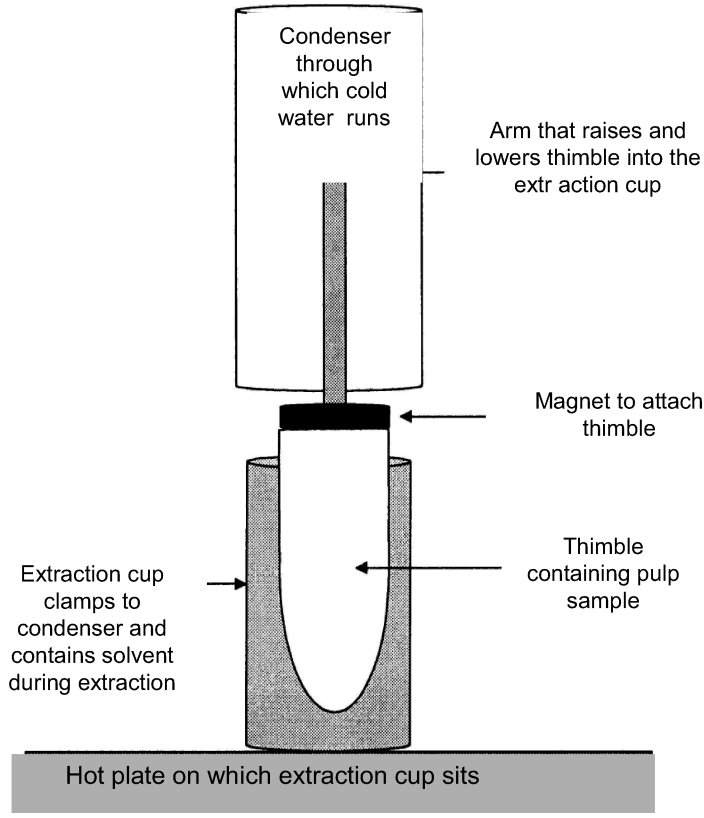

Figure 2. Schematic of a Soxtec extraction unit.

Randall's two-step extraction procedure reduced fat extraction time to less than one hour per sample. His research publications showed that the Randall extractor obtained results equivalent to Soxhlet with only 30 minutes of extraction time. Details of the operation of the Soxtec extractor have been reported.[6,7]

Soxtec extraction was performed on homogenized pulp samples using acetone as a solvent. Replicate 5 g samples were placed in cellulose extraction thimbles (24.5 mm i.d. × 26.0 mm e.d. × 60 mm length, Whatman(tm)) that were then attached to the magnets below the condensers in the Soxtec unit (Figure 2). When all samples were in place, extraction cups were placed on the hot plate below the thimbles and 70 mL of solvent were measured into each extraction cup and the extraction cycle was started by immersing the thimbles into the solvent. The hot-plate temperature was set to achieve a condensed solvent flow rate of three to five drops/s with the glass extraction cups. After boiling for one hour, the thimbles were raised out of the solvent and the rinsing operation was initiated.

During rinsing (for 30 minutes), the evaporated solvent from the extraction cups condensed when contacting the condensers, which had approximately 20°C cooling water running through them. The condensed solvent dripped down through the sample to rinse remaining lipids from the pulps into the extraction cups. After the rinsing duration, the lever on the Soxtec was moved into the solvent collection position to stop the solvent flow from the condensers back into the cups. The remaining solvent in the extraction cups was evaporated out of the cups and collected in the solvent reservoir of the Soxtec for later disposal.

When all of the solvent was evaporated out of the extraction cups as determined by visual examination, the cups containing the extracted lipids were removed from the Soxtec and the collected extracts were dried as per the methodology tested. The extracts were weighed on a microbalance.

Methylation for GC/MS Analysis

Each extract sample was reconstituted to a concentration of ~1000 ppm with methyl tertiary butyl ether:methanol (9:1). The samples were methylated using a diazomethane generating solution.[8] The methylated samples were then analyzed by gas chromatography/mass spectrometry (GC/MS).

Samples

The various extraction methods were evaluated on two sulphite pulp samples obtained from a dissolving pulp mill that used the ammonia process on softwood (spruce/balsam fir mix) furnish.

- A low-extractives pulp destined for pharmaceutical products
- A high-extractives pulp destined for non-pharmaceutical products

The pulps were received as dry sheets that had been collected from the warehouse. Portions were ccut into small pieces of about 1 cm^2 after which they were freeze-dried, and known weights (‘8 g) were then extracted.

Results

Low-extractives pulp. The results for analysis of the low extractives pulp are shown in Figure 3. The extractives content of the pulp are much lower than that typically found in kraft pulps (0.01% versus 0.2%). Hence, sample manipulation is likely to affect the repeatability of the data. Freeze-drying yields higher values in both Soxhlet and Soxtec extractions than the other modes of drying the extracts. This indicates that drying at higher temperatures results in loss of compounds due to volatilization or decomposition. In addition, freeze-drying of the extracts generates data with lower standard of deviations than the other

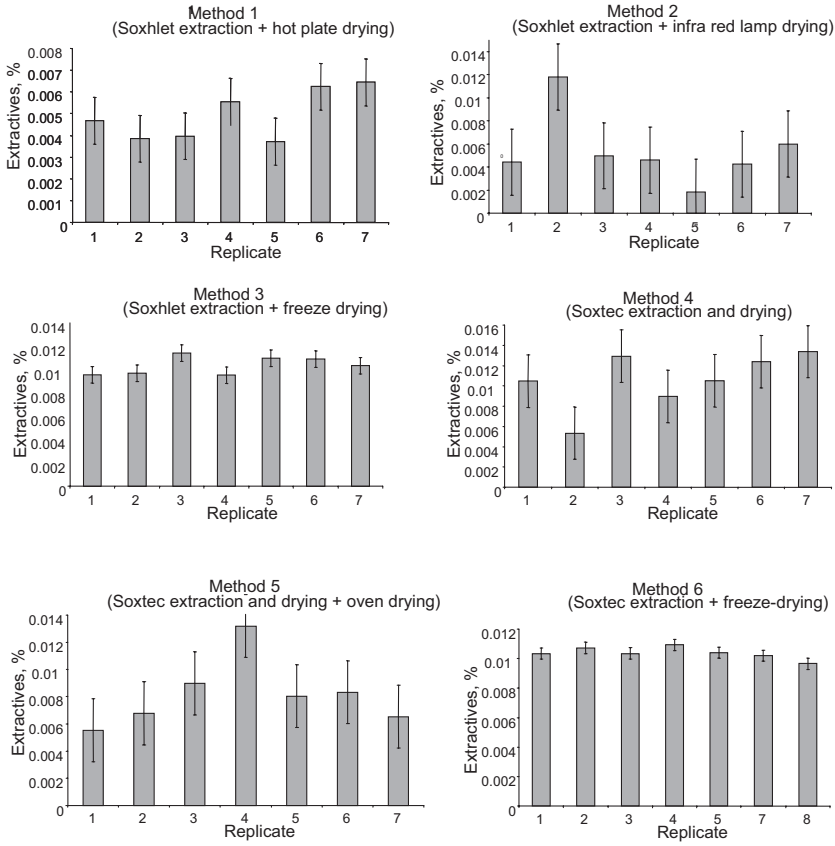

Figure 3. Results of replicate measurements of lipophilic extractives in a low-extractives dissolving pulp sample. Error bars show standard deviations of means.

drying modes. The results show that either Soxtec or Soxhlet extraction can be used but only the freeze-drying mode generates repeatable data. Unfortunately, freeze-drying capabilities are not available in laboratories of mills and their customers. This makes it hard to settle disputes when questions arise about the quality of low-extractives pulps.

Analysis of the extracts by GC/MS to ascertain the components present showed that only about 40% of the extracts were volatile enough to be analyzed by the technique. The major compounds identified were: fatty acids, carbamodithioic acid methyl ester, diethyldithiocarbamic acid, adipic dihydrazide, and adipic acid. In effect, most of the components present in the extracts were due to non-wood resin compounds, and are probably contaminants from sample collection and/or processing. For example, adipic acid, a component of nylon, could have originated from the felts used at the mill.

The major portion of the extracts is comprised of higher molecular weight material that cannot be determined by gas chromatographic techniques. This implies that normal efforts by sulphite pulp mills to further reduce the extractives content of the pulps may be in vain as they are aimed at targeting the low-molecular-weight, non-polymerized, lipophilic wood extractives. On the other hand, the wood extractives could have polymerized to form higher molecular weight compounds that are not extractable by conventional means. Indeed, reports have shown that polymerization of wood extractives does occur.[9–12] In that case, the polymerized wood resin will not be amenable to removal by methods targeted for normal wood resin compounds.

High-extractives pulp. The results for analysis of the high-extractives pulp are shown in Figure 4. Although this is considered to be a high-extractives

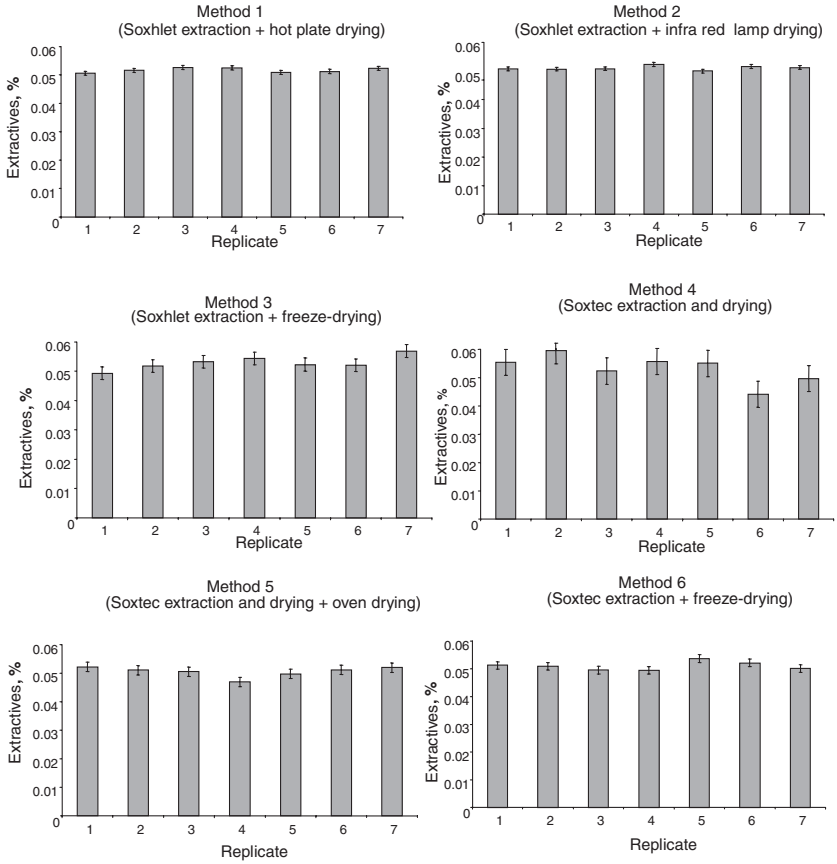

Figure 4. Results of replicate measurements of lipophilic extractives in a high-extractives dissolving pulp sample. Error bars show standard deviations of means.

content pulp, it is clear from the data that the values are still lower than those typically found in kraft pulps (0.05% versus 0.2%). Overall, the amounts of extractives obtained from the different extraction schemes are comparable. Also, the methods have narrow standard deviations. This implies that any of the methods can be used to generate repeatable data.

Analysis of the extracts by GC/MS showed that the components present were mainly fatty acids, resin acids, sterols, and erucylamide. These are all wood resin components except for erucylamide, which is commonly used as an antiscaling or release agent in the manufacturing of plastics. Unlike in the case of the extracts from the low-extractives pulp, the GC/MS analysis was able to detect only about 10% of the extracts. Thus, the major portion of the extracts is comprised of higher molecular weight material that cannot be determined by gas chromatographic techniques. It is possible that the extra measures taken at the mill to produce the low-extractives pulp removed or degraded some of the polymerized matter.

PART 2. FATE OF LIPOPHILIC EXTRACTIVES

The best extraction method found in Part 1, namely, Soxtec extraction with freeze-drying, was used to characterize and profile lipophilic extractives in different unit operations of two sulphite pulp mills. It was hoped that the information gained from the profiling would shed light on the best approaches to use to lower the extractives content of the final pulps. A useful preliminary approach is to analyze and characterize the extractives in the incoming furnish and the final product. Accordingly, we analyzed the incoming wood chip furnish and final pulp samples from one mill and then conducted a profile of lipophilic extractives across the fiber line of another. This part of the study used pulps destined for products that tolerated higher levels of extractives than those used in Part 1.

Samples

The following samples were obtained.

Mill A: Ammonia Sulphite Pulping

1. Fresh chips and concomitant final pulp.
2. Seasoned chips (six weeks in a chip pile in the summer) and concomitant final pulp.

The chip samples were comminuted and then freeze-dried before solvent extraction with dichloromethane. Dichloromethane was used because it is the solvent of choice in laboratories of sulphite mills and their customers. The pulp samples were shredded into small pieces and also extracted. The extracts were weighed and then analyzed to ascertain their composition.

Table 1. Time-line sequenced collection of samples at a sulphite mill

Sample #	Sampling point
1*	Inlet chips
2*	Blend tank pulp
3*	Thickener #1
4	Thickener #2
5	Dc washer #2 vat
6*	Cl_2 washer outlet
7	Frotapulper A #1
8	Frotapulper A #2
9	Caustic tower inlet
10	EP washer inlet
11	EP washer #1
12	EP washer #2
13	ClO_2 tower outlet
14	H tower inlet
15*	H washer vat
16	Hypo washer
17	Storage tank
18*	Final pulp

*Selected for more detailed analyses by GC, GC-MS, and SEC.

Mill B: Magnesium Sulphite Pulping

Samples were collected from a number of unit operations in the mill as listed in Table 1. The samples were collected in time-line sequence to ensure that the fate of the incoming chip furnish was followed through the mill operations. Portions of the samples were freeze-dried and then extracted with acetone on a Soxtec unit. Samples whose numbers have asterisks, namely, 1, 2, 3, 6, 15, 18, were selected for more detailed analyses by GC, GC/MS, and SEC (size exclusion chromatography). Sampling points 3, 6, and 15 were prone to pitch deposition and required continual addition of an additive to minimize the deposition. The final pulp (sample 18) caused pitch deposition during papermaking. Thus it would be very informative to ascertain which components in the extractives are the main culprits of the deposition.

Experimental

GC-FID Analysis

The GC analyses were performed on a Varian 3900 GC equipped with a CP-8400 autosampler. The separation was on a fused silica capillary column (DB-5HT, J & W; 30 m $\times$ 0.25 mm I.D. $\times$ 0.10 μm). The oven was heated from

125°C to 360°C at 6°C/min and held for 25 minutes. The injector (split-splitless) and flame ionization detector temperatures were set at 360°C and 370°C, respectively. The injection was performed in both split (100:1, 50:1, 25:1, 10:1) and splitless modes. Helium was used as a carrier gas. Data processing was performed on a Varian Star Chromatographic Workstation, version 6.20.

A mixture of standard compounds was used in a concentration range from 50 to 200 ppm for identification and quantification purposes. Standard compounds are grouped as their representative classes, namely, Fatty Acid Group (palmitic acid, linoleic acid, oleic acid, stearic acid, and stearolic acid), Resin Acid Group (pimaric acid, levopimaric acid, neoabietic acid, dehydroabietic acid, abietic acid, and henecosanoic acid), Fatty Alcohol Group (behenic alcohol), Sterol Group (campesterol, stigmasterol, β-sitosterol), Steryl Ester Group (palmitic acid steryl ester, stearic acid steryl ester, and behenic acid steryl ester, cholesterol stearate), and Glyceride Group (tricaprin, distearin, dipalmitin, distearin, trimyristin, tripalmitin, tristearin, triheptadecanoin, and trinonadecanoin). The procedure has been described before.[13] The compounds were obtained from Sigma-Aldrich with purities ranging from 95% to 99.5%. Each of the standard compounds was analyzed individually by GC-FID and corrected for its purity.

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 10^7, 10^6, and 10^5 Daltons, 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

Mill A: Ammonia Sulphite Pulping

Results for lipophilic extractives contents of the extractives of the chips and pulp samples are shown in Table 2.

The results show that fresh chips contain high lipophilic extractives (3.65%) that result in high lipophilic extractives in the final pulp (0.34%). Thus, the unit operations removed 90.9% of the lipophilic extractives in the incoming fresh chips. Using seasoned chips results in a lowering of the lipophilic extractives in the final pulp (0.13%). This confirms that wood seasoning is an effective way of reducing lipophilic extractives in all pulp and papermaking operations.[1] However, in this case the unit operations removed 85.8% of the

Table 2. Lipophilic extractives in chips and final pulp samples (% extractives)

Sample	Total DCM eExtracts
Fresh chips	
Chips	3.65
Pulp	0.34
Seasoned chips	
Chips	1.34
Pulp	0.13

extractives in the incoming furnish. GC analysis shows that the eluted matter accounted for about 39% of the extracts from the chips and for only 6% of the extracts from the pulp samples. This raised questions about the nature and chemistry of the components that did not elute through the GC analytical column.

Mill B: Magnesium Sulphite Pulping

Results for the profile of the lipophilic extractives from several unit operations in the mill are shown in Figure 5. The data show the following:

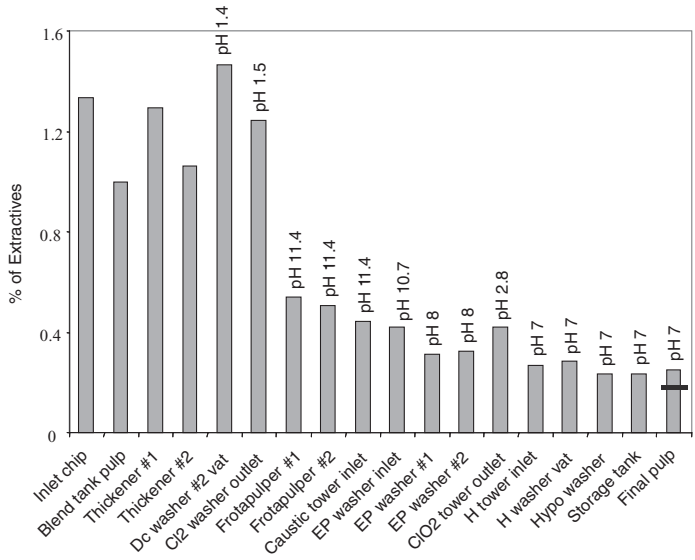

Figure 5. Profile of lipophilic extractives along a magnesium sulphite fiber line. The solid line indicates the targeted value.

1. It is evident that the amount of extractives decreases along the fiber line from the chips to the finished product (from 1.3% in the chips to 0.31% in the final pulp).
2. There is about 25% removal of extractives in the digester.
3. After the digester, the amounts of extractives increase and remain high right up to the Cl_2 washer outlet. This is a reflection of the mill process where there is recirculation of the wash water from the washer #2. The acid conditions do not affect the lipophilic extractives chemistry (e.g., the fatty and resin acids are protonated and the glycerides are not degraded). Consequently, there is no removal of the extractives in the washing and thickening stages.
4. The amounts of extractives in the pulp decrease significantly after the pulp has been in alkaline conditions (starting at the Frotapulpers). In this case, the basic conditions cause degradation of glycerides and formation of soluble sodium soaps of fatty and resin acids that are removed during the washing and thickening stages.
5. The lipophilic extractives content of the final pulp indicate that the unit operations in this mill resulted in 85% removal of the extractives that came in with the incoming furnish.
6. However, the extractives in the final pulp are 25% higher than targeted by the mill (as indicated by the solid line on the chart). The high lipophilic extractives content is a reflection of the use of fresh unseasoned wood and, probably, inefficient operation of unit operations that affect removal of wood resin. These include Frotapulpers, washers, and thickeners.

GC Analysis

Detailed characterizations of the components present in the extractives from 5 of the sampling points are shown in Figure 6.

The results show that:

1. The predominant components in the chip extracts are glycerides, fatty acids, resin acids, and sterols. Glycerides, fatty acids, and sterols occur in about the same concentrations.
2. The same compounds predominate in the blend tank and Cl_2 washer samples. However, here the concentrations of the glycerides are much more predominant relative to the other components. The concentrations of all the components fall dramatically after the pulp has been in alkaline unit operations.
3. It is evident that glycerides and sterols are the major components in the final pulp. This indicates that any moves to further reduce the extractives in the final pulp should target these components.
4. The preponderance of glycerides and sterols in the chlorine washer outlet and H washer vat samples probably explains why these unit operations are

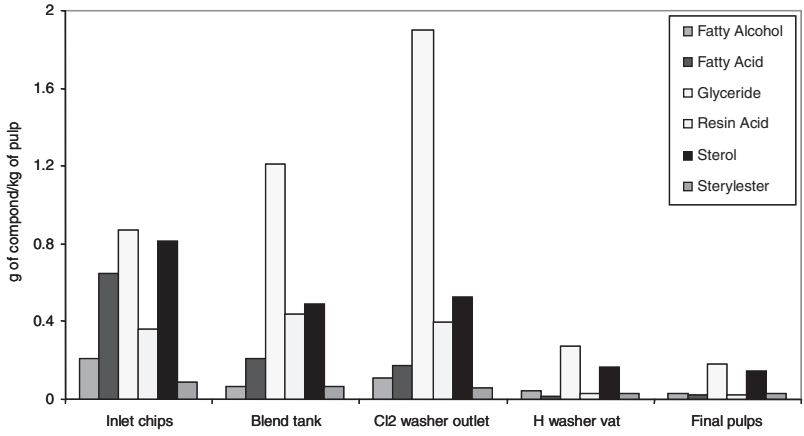

Figure 6. Components identified in lipophilic extracts of samples from a magnesium sulphite fiber line. Glycerides refer to triglycerides that are esters of fatty acids.

prone to pitch deposition, as glycerides and sterols are commonly found in pitch deposits.

5. Extractives of the final pulp also contain elevated amounts of glycerides and sterols, thus accounting for the deposition problems on the paper machine.
6. These observations are based on about 10% of the material from the extractives that eluted through the GC column. Evidently, the majority of the components in the extractives are comprised of material other than common wood resin compounds.

SEC Results

To better understand the chemistry of the lipophilic extractives, extracts from several samples were analyzed by SEC. The results are shown in Figures 7 and 8. In the extracts from the ammonia process, we see that there is a significant amount of polymerized material that elutes before the triglycerides (in the standard mixture). Indeed, the calibration standard indicates that the molecular weight of this matter is in the 2000–11,000 Daltons range. All the different grades of sulphite pulp produced at this mill display the same molecular weight profiles, indicating that the unit operations affect the chemistry of the extractives in the same manner irrespective of the grade produced. It appears that the unit operations in the mill processes cause extensive polymerization of the lipophilic extractives. This explains the low amounts of volatile matter in the extracts that were amenable to analysis by GC.

The SEC profiles of samples from magnesium sulphite pulping are shown in Figure 8. Here we see that the chromatograms of the inlet chips and the final pulp match each other except for the presence of a hump in the final pulp

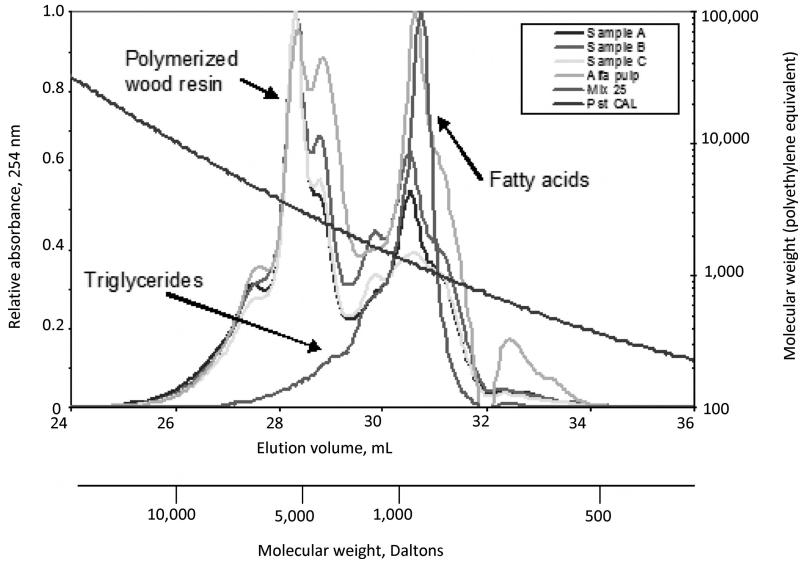

Figure 7. SEC profiles of lipophilic extractives from ammonia sulphite pulp (Samples A, B, and C are different grades of final pulp; Alfa pulp is a low-extractives dissolving pulp; Mix 25 is a mixture of 25 individual standards used in quantification of lipophilic extracts by GC; Pst CAL is a polystyrene calibration standard).

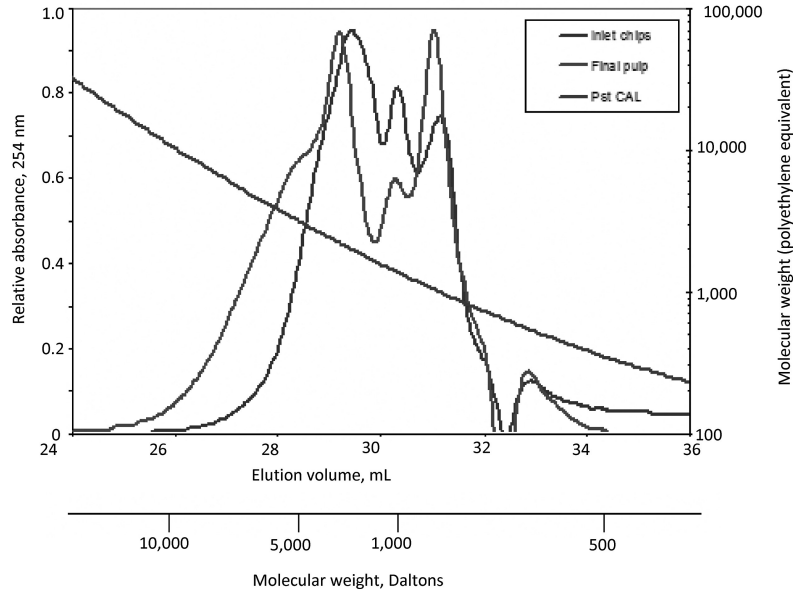

Figure 8. SEC profile of lipophilic extractives from magnesium sulphite pulp.

extracts that is indicative of the presence of high molecular weight matter. Thus it appears that some unit operation(s) in the mill process induced significant polymerization of the lipophilic extractives.

CONCLUSIONS

In the pulp that contains a low level of extractives, drying of extracts by freeze-drying gave the more repeatable results and lower standard deviation than that using heat aided drying. Either Soxhlet or Soxtec extraction can be used, but the latter is more rapid and easier to use. Since most mill laboratories do not have freeze-drying capabilities, it is apparent that using normal drying techniques may not be sufficient to resolve disputes between mills and their customers about the amounts of residual extractives in the final pulps.

Results for the pulp that contains high level of extractives show that any of the drying techniques evaluated can give reliable data. This is good news for mills laboratories that are not equipped with freeze-drying capabilities.

Glycerides and sterols are major components in both the ammonium and magnesium sulphite processes. This indicates that further reductions in lipophilic extractives contents of the final pulps can be achieved by implementation of processes or methods that target these compounds.

It appears that lipophilic extractives from ammonium sulphite pulps contain more polymerized matter than the extractives from the magnesium process. This probably indicates that the ammonia process is more conducive to polymerization of the extractives than the magnesium process.

It is important to note that the SEC data will require further clarification by other analytical techniques such as liquid chromatography/mass spectrometry (LC/MS) that will yield unequivocal information on the structure and molecular weight of the components present in the lipophilic extracts. For example, since unsaturated fatty acids and glycerides are not UV active, what is the exact composition of the compounds that are observed in eluates of the SEC? Are they resin acids attached to the polymerized wood compounds? These questions will be answered by analysis of the extracts using LC/MS, a technique that can facilitate analysis of high molecular weight compounds.

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