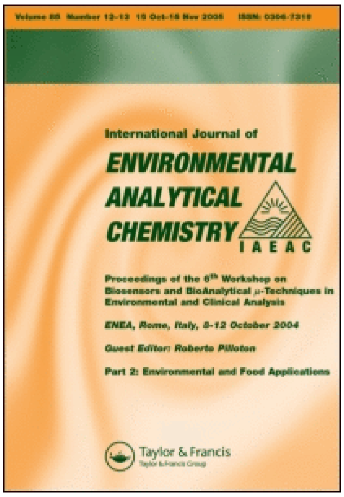

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A COMPARATIVE STUDY OF CHEMITHERMOMECHANICAL AND KRAFT WOOD PULP EXTRACTS

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Wood pulp mill effluents continue to attract much attention due to environmental consequences. However, in comparison, very little work has been published on wood pulp extracts. In this study chemithermomechanical pulps (CTMP) as well as Kraft (sulphate) pulps were Soxhlet-extracted with three solvents of different polarity. Per cent extractives into the three solvents per air dried wood pulp were used as one of the bases for comparison. Analysis by gas chromatography (GC) using both a flame ionization detector (FID) and a mass selective detector (MSD) was performed. Significantly greater quantities of volatile extract were found with CTMP pulps than with Kraft pulps.

INTRODUCTION

The characterization of wood pulps, like all natural products, is complicated by the complexity and inhomogeneity of the materials. Wood extractives have been found to consist principally of hydrocarbons, alcohols, acids, esters, ketones, lipid substances, waxes, terpenoids and phenolics[1–3]. Many of these species survive the pulping and bleaching processes and hence are found as wood pulp extractives. The extractive content varies, depending on the pulping process utilized and the method of bleaching employed[4]. Furthermore, other factors like the type of tree from which the wood originated, the age of the tree, whether the wood chips were subjected to a pre-hydrolysis step before either pulping or bleaching, the season in which the tree was cut down and if the wood chips were stored before pulping[5] may be important.

Since 1967 there have been a number of articles published on wood extractives as well as pulp mill effluents; however, wood pulp extractives have comparatively received little attention. So far wood pulp extractives have mainly been studied in order to determine the origin and extent of resin-speck formation as well as colour reversion in tropical[6–12] and temperate[13–15] wood Kraft pulps. In another study, Chapman *et al.*[16] have attempted to examine the non-structural chromophoric substances in a bisulphite pulp. Later the gas phase above several pulp samples was analyzed by capillary gas chromatography using Kovats indices[17]. In 1967, after stepwise extraction, the resin content of unbleached (UBKP) and bleached prehydrolysis Kraft pulp (BKP) was studied. Separation was accomplished on silica gel with subsequent off-line identification by NMR. The UBKP extract contained traces of fatty acids and β-sitosterol, while the BKP extract contained acids and other oxidized substances. A modified sterol considered to be less hydrophobic than β-sitosterol was also found[18].

The usefulness of thin-layer chromatography (TLC) for rapid analysis of non-volatile compounds found in Kraft pulp extractives has been discussed[19]. Examples of TLC potential with varying solvent systems were given. In another study involving extractives of Kraft pulps, 14 triterpenoids, 4 steroids and 2 fatty alcohols were isolated by HPLC using a combination of gel-permeation, reversed-phase and silica gel columns[20]. ^{13}C-NMR spectroscopy was employed via several pulsed methods to aid in structural identification.

The first study published regarding the analysis of mechanical pulp extracts is as recent as 1989[21]. Herein, detailed analysis of the lipophilic and polar pulp extractives was performed using capillary GC-MS. Dichloromethane extraction followed by another extraction with water-acetone (1:9) was performed. The extractant was then derivatized, separated on a polymethylsiloxane column with heptadecanoic acid as the internal standard. For all the pulps studied, free and esterified fatty acids, sterols and resin acids together comprised over 80% of all the lipophilic extractive components.

From an environmental standpoint, it is of interest to ascertain the nature and abundance of as many compounds present in pulp extracts as possible, bearing in mind that these components occur at low concentrations. To date, the extraction of pulps has been done by either extracting a single sample with different solvents in a stepwise treatment technique[9,11,12,14,18,20] or by performing several extractions with fresh sample of the same pulp each time but with different solvents[6,7,13]. The latter method has been adopted in the study of CTMP and Kraft pulps reported here, since it was believed that the former method would be cumbersome, time-consuming and runs the risk of modification of the extractives by virtue of the fact different solvents would be used with the same pulp sample. Three extracting solvents were selected primarily based on their different solvent strengths, with cyclohexane being the least polar (μ, ca. 0 debyes), water being the most polar (μ, ca. 1.85 debyes) and ethyl acetate having an intermediate polarity (μ, ca. 1.78 debyes). GC-MS was next performed on many of the carefully isolated extractant mixtures in order to estimate the chemical differences between volatile components in CTMP and Kraft pulp extracts.

EXPERIMENTAL

The six pulps used for this study are listed in Table I, together with their backgrounds. CTMP-I and CTMP-II are pulps bleached by the peroxide process, while BKP-I, BKP-II and BKP-III are pulps bleached by the multistage chlorination process. UBKP-I is the Kraft pulp that was not subjected to the bleaching process.

The extraction solvents used were ethyl acetate, HPLC-grade purchased from B&J; cyclohexane, HPLC-grade purchased from Fisher Scientific, and distilled-deionized

Table I Background of pulps studied.

Wood pulp	*Wood source*
CTMP-I[a]	Northern Softwoods
CTMP-II[a]	Northern Softwoods
UBKP-I[b]	Southern Softwoods
BKP-I[c]	Southern Softwoods
BKP-II[c]	Southern Softwoods
BKP-III[c]	Northern Softwoods

[a] Chemithermomechanical pulp.
[b] Unbleached Kraft pulp.
[c] Bleached Kraft pulp.

water. All the glassware used for these extractions was washed well, rinsed three times in distilled water, oven-dried and, where applicable, stored in a grease-free desiccator.

Soxhlet extraction procedure

The Pyrex brand glass thimble with a fritted disc of coarse porosity purchased from Fisher Scientific, together with the magnetic stirring bar and the glass stopper were first pre-extracted in about 300 ml of the respective solvent for about 12 h. Next, as shown in Fig. 1, about 16 g of the pulp which was previously weighed in an aluminium boat, was carefully transferred into this pre-extracted thimble. the aluminium boat was re-weighed to determine the exact weight of the pulp transferred. The pre-extracted flask was rinsed three times with the respective fresh solvent and then exactly 300 ml of the same fresh solvent were added to this flask. Soxhlet extraction for 72 h was carried out at approx. 77°C for ethyl acetate, 81°C for cyclohexane and 100°C for water. During the extraction, the Soxhlet thimble was wrapped in thermal felt in order to maintain a constant temperature. Each subsequent Soxhlet extraction was preceded by a pre-extraction in order to erase any memory effects from the previous extraction. Blank extractions with each solvent using the pre-extracted glassware were carried out following the same procedure as in Figure 1, but without the pulp in order to account for the background.

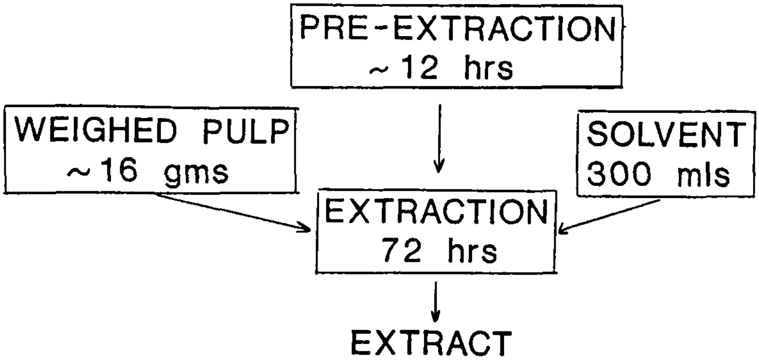


Figure 1 The procedure for Soxhlet extraction.

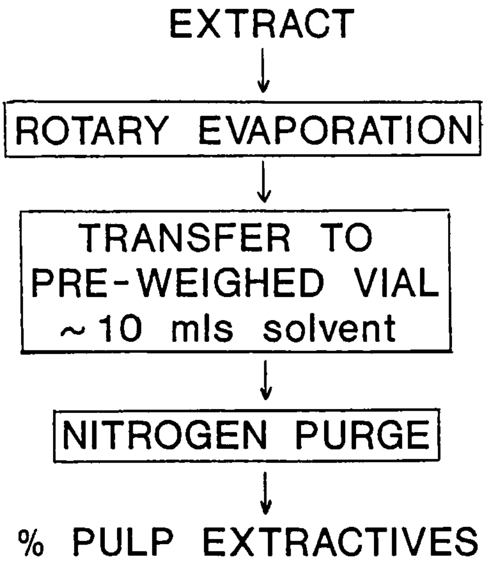


Figure 2 The procedure for concentrating and drying of the extracts.

After the extraction was completed, in the case of ethyl acetate and cyclohexane, the extract was concentrated to about 10 ml in a grease-free rotary evaporator under vacuum. With water as the extraction solvent, this step was accomplished by forming an azeotropic mixture with HPLC-grade methanol. All concentrated extracts were carefully transferred to previously weighed glass vials and dried with the aid of a slow stream of pre-purified nitrogen. The flow chart regarding this procedure is shown in Figure 2. The dried extract was then accurately weighed on an analytical balance and the per cent extractives calculated after subtracting the background. A duplicate extraction was performed for each pulp in each solvent.

Analysis

The dried extracts were dissolved in a small quantity of their extraction solvent, filtered if necessary and the resulting solution was used for analysis by GC/FID and GC/MS. Only ethyl acetate and cyclohexane extracts were used for analysis by GC/FID, whereas all the three solvent extracts of the above mentioned pulps were analyzed by GC/MS.

GC/FID

Separations were performed with a Model 5890A gas chromatograph (Hewlett-Packard) equipped with FID and a splitless/split capillary column inlet system. A 10 m × 0.2 mm i.d., 0.25 μm film-thickness, SE-54 bonded-phase fused silica capillary column coated with 5% diphenyl-94% dimethyl-1% vinyl polysiloxane was used. Helium was used as the carrier gas with linear velocity of 22 cm/sec. Nitrogen served as the make-up gas. The detector and injector were set at 280°C. The temperature programme employed was as follows: initial oven temperature, 60°C for 1 min; ramp at 8°C/min until 280°C; finally hold at 280°C for 10 min. For the ethyl acetate and cyclohexane extracts 1 μl of reconstituted solution was injected. All the injections were done manually with a Hamilton Microliter Syringe. All the data were recorded by a Hewlett-Packard 3392A integrator.

GC/MS

Mass spectra were obtained by direct interface of the above gas chromatograph with a Model 5970 (Hewlett Packard) Mass Selective Detector. The transfer line was maintained at 250°C with helium as the carrier gas. The capillary column, injector temperature of the capillary inlet system and temperature ramp were the same as mentioned previously for GC/FID. The mass spectra were obtained in the electron impact (EI) ionization mode at an electron beam energy of 70 eV. The ion source temperature was maintained at 200°C and the mass scan range was 50–450 amu. The volumes of the extracts injected were identical to that used in GC/FID. All the data were processed using an HP 59970C Chem Station.

RESULTS AND DISCUSSION

Attempts were made to carry out all extractions with utmost care. Glass thimbles and stoppers were washed and rinsed in distilled-deionized water and dried in an oven prior to use. They were carefully wrapped in tissue and stored in a grease-free desiccator to avoid any dust or grease. After the pre-extractions were completed, care was taken not to touch any of the pre-extracted materials by hand. Extractions were carried out immediately after the pre-extractions were done in order to minimize any contamination due to long standing or storage. The transfer of the pulps into the thimbles was a painstaking task, due to the physical nature of the pulps. Care was taken to pack as much as possible with minimum losses. The pre-extracted flask was rinsed three times with fresh solvent before adding the final 300 ml. Every Soxhlet extraction was preceded by a pre-extraction of the system with the respective extraction solvent. Concerning the extractant concentration and drying procedures, the rotary evaporator used was grease-free.

Duplicate extractions were carried out for each pulp in each solvent with very good reproducibilities (Table II). Per cent water extractives were the highest, followed by ethyl acetate and cyclohexane extractives. A similar trend has been observed for wood extractives of several tropical wood species[22,23]. The water extracts were hygroscopic; after a span of one month, their weights increased. CTMP water extractives were much higher in content than the Kraft water extractives. A plausible explanation could be the higher content of lignin in CTMP pulps which degrade on being bleached. The pH of an extract can determine the form in which a compound exists in an extract[24,25]. The pH of all the water extracts was found to be 6.0 with the exception of UBKP-I with a value of 10.0 and BKP-I having a pH of 6.5. CTMP

Table II Per cent extractives per air-dried wood pulp.

Wood pulp	*EtOAc*	C_6H_{12}	H_2O
CTMP-1	0.12	0.05	2.58
	0.14	0.05	3.45
CTMP-II	0.13	0.04	3.20
	0.11	0.06	4.05
UBKP-1	0.05	0.05	1.73
	0.08	0.02	1.57
BKP-I	0.01	0.01	0.92
	0.02	0.01	0.74
BKP-II	0.04	0.03	0.80
	0.04	0.03	0.83
BKP-III	0.23	0.13	0.44
	0.22	0.14	0.44

ethyl acetate extractives were slightly higher than Kraft ethyl acetate extractives with BKP-III being an exception. In the case of the cyclohexane extractives, BKP-III had the highest value while the per cent extractives of the remaining pulps (CTMP and BKP) were about the same. On comparing the UBKP-I and BKP-I per cent extractives, the former was greater in value no matter what solvent was employed. This indicated that the multistage bleaching process reduced the extract content for all polarities.

Analysis by GC/FID was first done to gauge the number of different components in each pulp extract since FID is known to be responsive to most organic materials. Per cent extractive does not necessarily indicate a wide variety of components. While an open tubular capillary column was employed, our goal was not to examine thoroughly as many components as possible, but to compare under identical conditions Kraft pulps and CTMP pulps. For this reason, we did not choose to derivatize (e.g. silylate) components to enhance volatility. For example, many more different volatile components are extracted with cyclohexane from CTMP-II (Figure 3) than from UBKP-I (Fig 4) even though the per cent extractives were similar. On the other hand, the number of volatile compounds extracted from BKP-I (Figure 4) with cyclohexane was smaller than that extracted from UBKP-I (Figure 5) which was similar to our observation regarding the magnitude of per cent extractives. Similar trends were observed with ethyl acetate as the extraction solvent. Of course these data do not allow our drawing any conclusions concerning semi-volatile and non-volatile extracted components.

Analysis of the total ion current chromatograms obtained under the same GC conditions with MSD for the different extracts reinforced some earlier GC/FID conclusions. Again, our goal was not to perform an exhaustive examination of as many components as possible in these extracts but, rather, to show in a qualitative manner the differences and commonality of CTMP and Kraft pulp extracts. Figs 6 and 7 which are for ethyl acetate extracts of CTMP-I and BKP-I, are illustrative of these data. Peak number designation is given in Tables III, IV and V. These assignments were made based on an NBS Library search with a probability match

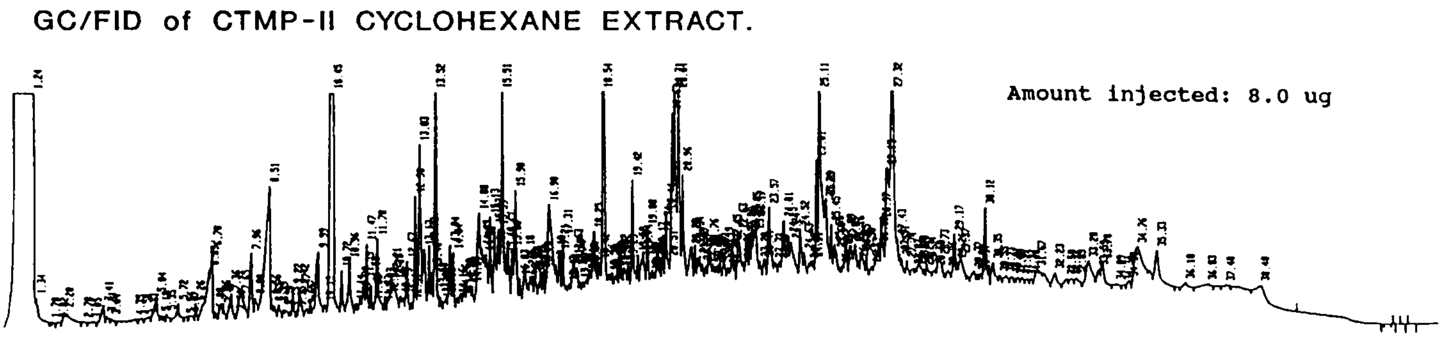


Figure 3 GC/FID of CTMP-II cyclohexane extract. Injector: splitless/split at 280°C; column: SE-54 (10 m × 0.2 mm i.d.), 0.25 μm film thickness. Carrier: helium; make-up gas: nitrogen; detector: FID at 280°C. Temperature programme used was 60°C for 1 min, then a ramp of 8°C/min until 280°C where the temperature was kept constant for 10 min: 1 μl injections.

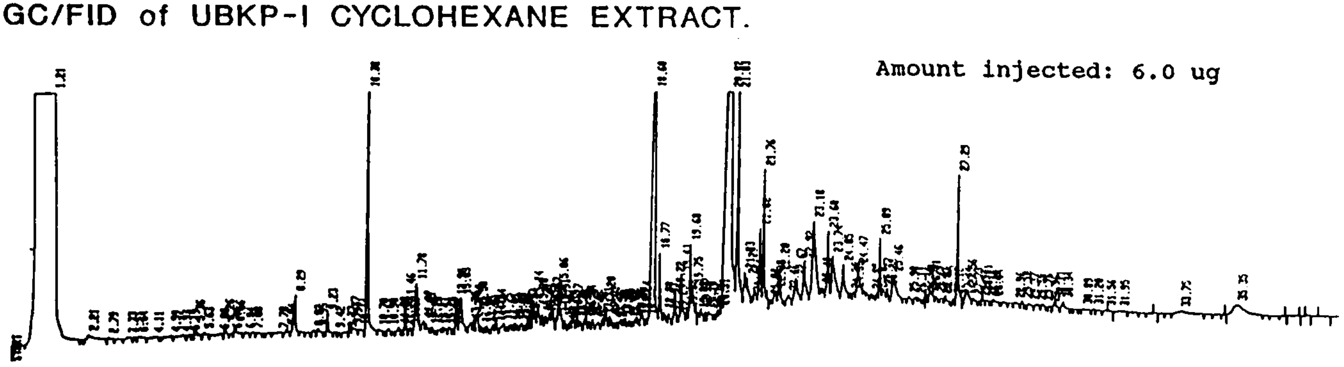


Figure 4 GC/FID of UBKP-I cyclohexane extract. Conditions same as in Figure 3.

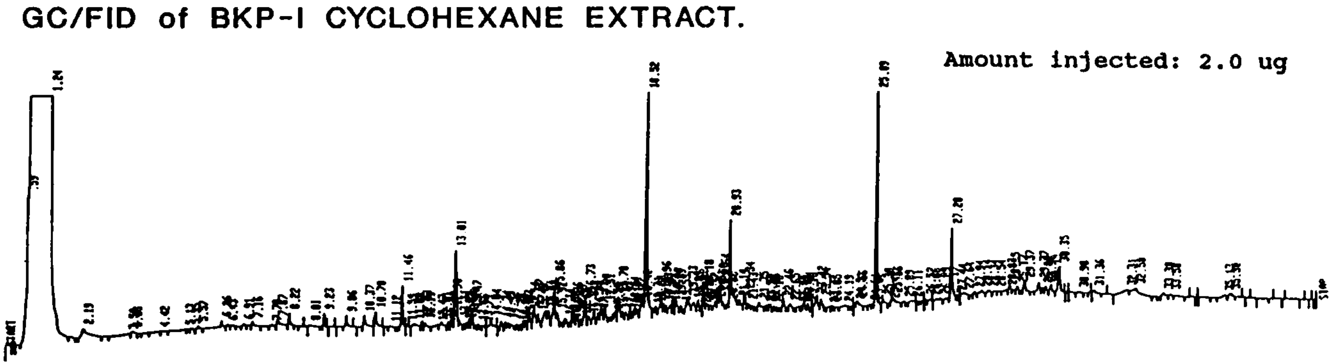


Figure 5 GC/FID of BKP-I cyclohexane extract. Conditions same as in Figure 3.

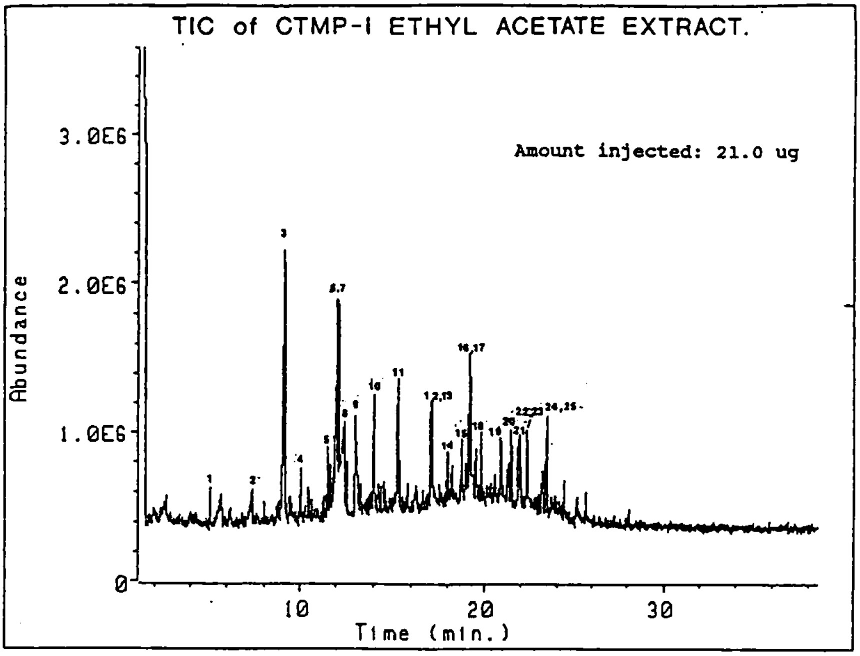


Figure 6 GC/MS of CTMP-I ethyl acetate extract. Conditions of GC same as above. Transfer line: 250°C; injection: 1 μl. Electron impact ionization used for ion production. Beam energy, 70 eV. Mass range monitored, 50–450 amu.

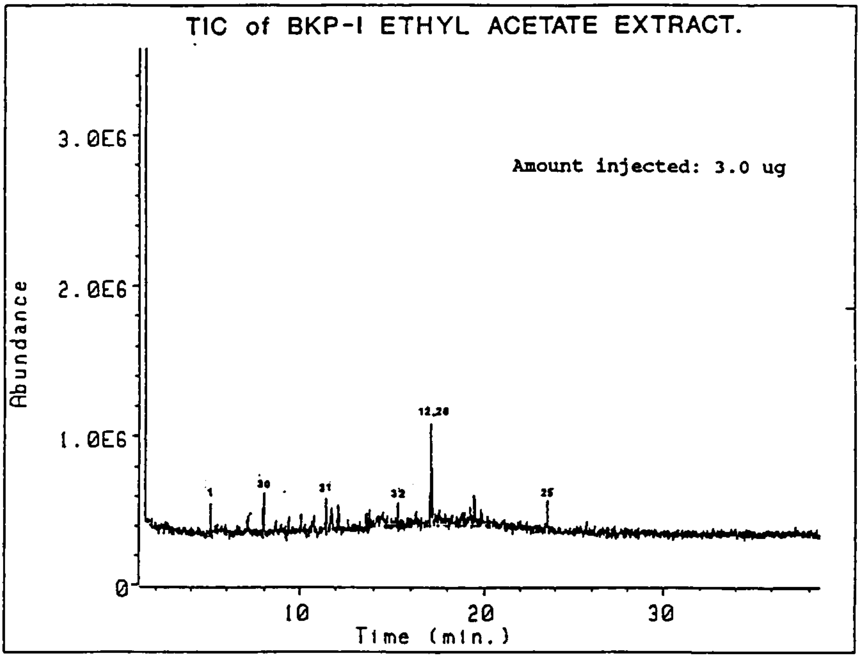


Figure 7 GC/MS of BKP-I ethylacetate extract. Conditions same as Figure 6.

Table III Major peak assignments for select extracted wood pulp components[a].

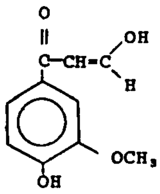
Peak number	CTMP-I			CTMP-II			UBKP-I			BKP-I			Assignment
	EA	*CH*	*W*	*EA*	*CH*	*W*	*EA*	*CH*	*W*	*EA*	*CH*	*W*[b]	
1	y			y			y			y			Decamethylcyclopentasiloxane
2	x			x									Long chain (fatty) acid[c]
3	x	x	x	x	x	x	x	x					4-Hydroxy-3-methoxy benzaldehyde(Vanillin)
4	x												2-Methoxy-4-propyl phenol
5	x												Phenol[c]
6	x			x									1-Propenone, 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)[d]
7	x	x		x	x								Ketone[c]
8	x												4-Hydroxy-3-methoxybenzoic acid(Vanillic acid)
9	x		x	x									4-Hydroxy-3-methoxybenzene-acetic acid
10	x	x		x	x								Phenol[c]
11	x			x									1-propanone, 3-hydroxy-1-(4-Hydroxy-3-methoxyphenyl)[e]
12	y	y		y	y					y	y		1,2-Benzenedicarboxylic acid diisobutyl ester
13	x				x		x	x					Aliphatic ester[c]
14	x												Long chain aliphatic[c]
15	x												Saturated hydrocarbon[c]
16	x												Unsaturated aliphatic ester[c]
17	x	x											9-octadeconoic acid (oleic)
18	x												Saturated hydrocarbon[c]

[a] x = component of pulp was found in extract; y = impurity found in extract.

[b] EA = ethyl acetate extract, CH = cyclohexane extract, W = water extract.

[c] Chemical class, specific compound unspecified.

[d]



[e]

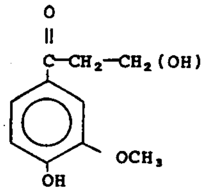


Table IV Major peak assignments for select extracted wood pulp components[a].

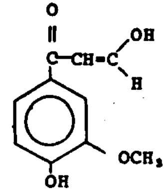
Peak number	CTMP-I			CTMP-II			UBKP-I			BKP-I			Assignment
	EA	*CH*	*W*	*EA*	*CH*	*W*	*EA*	*CH*	*W*	*EA*	*CH*	*W*	
19	x												Aliphatic ester[c]
20	x												Hexanedioic acid, dioctyl ester(adipate)
21	x												Sterol[c]
22	x												Phenol[c]
23	x												1-Phenanthrenecarboxylic acid ester
24	x	x											Monoalkyl benzene[c]
25	y	y		y	y		y			y			Dioctyl benzenedicarboxylic ester
26				x									Phenol[c]
27				x									Unknown
28		x		x						x			Octadecenois acid ester (oleic)
29		x		x	x								Aliphatic ketone[c]
30										y			Dodecamethylcyclohexasiloxane
31										x			Phenyl isoindole dione[c]
32										x			Steroid[c]
33							x	x					Unsaturated fatty acid[c]

[a] x = component of pulp was found in extract; y = impurity found in extract.

[b] EA = ethyl acetate extract, CH = cyclohexane extract, W = water extract.

[c] Chemical class, specific compound unspecified.

[d]



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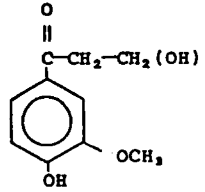


Table V Major peak assignments for select extracted wood pulp components[a].

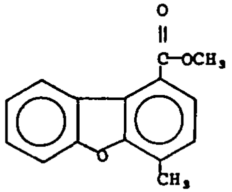
Peak number	CTMP-I			CTMP-II			UBKP-I			BKP-I			Assignment
	EA	*CH*	*W*	*EA*	*CH*	*W*	*EA*	*CH*	*W*	*EA*	*CH*	*W*	
34						x	x	x					Long chain aliphatic[c]
35						x	x		x				Unknown
36		x											Sterol[c]
37					x								Long chain aliphatic[c]
38								x					Dehydroabietic acid
39								x					Methyl 4-methyl-dibenzofuran-1-carboxylate[d]
40								x					1-Hexadecanol
41			x										Formic acid
42			x			x					x		3-Hydroxy-2-butanone
43			x			x					x		1-Hydroxy-2-propanone
44			x			x					x		Aliphatic compound[c]
45			x			x					x		Aliphatic aldehyde[c]
46			x										2-Furan methanol
47			x			x					x		Ketone[c]
48			x										Cyclohexanone
49			x			x							2-Cyclopenten-1-one, 2,3,4,trimethyl
50			x			x						x	Unknown
51			x			x							4-Hydroxy-3-methyl acetophenone
52						x							Primary alcohol
53						x							1,2,-Cyclopentanedione, 3-methyl
54						x							Cholestane diol[c]

[a] x = component of pulp was found in extract.

[b] EA = ethyl acetate extract, CH = cyclohexane extract, W = water extract.

[c] Chemical class, specific compound unspecified.

[d]



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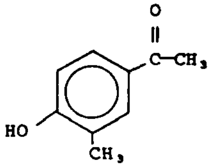

of more than 95% and further confirmation by a manual search[26]. As can be observed, it was possible to identify only about 50% of the total peaks detected in the four extracts studied. For the remaining peaks a confident, reasonable assignment was not possible without appropriate standards. However, based upon our interpretation of each spectrum and the general class of compound indicated as the 'best hits' from the computer search, most of these peaks could be given a chemical class designation. A general inspection of the GC/MS results again indicate that CTMP pulp extracts contain appreciably more volatile components than either bleached or unbleached Kraft pulp extracts.

A few of the fully identified peaks turned out to be impurities (designated by 'y') which are believed to be due to sample handling. These impurities can be accounted for, but their presence was surprising in light of the extreme care with which the study was undertaken. It is believed that peaks 12 and 25 probably arose from plasticizers in plastic bags that were used for storage of the wood pulps. It is assumed that the source of peaks 1 and 30 could be grease, wax or rubber tubing used in sample manipulation. Decamethylcyclopentasiloxane (Peak 1) was found in the ethyl acetate extracts of all the pulps. Dodecamethylcyclohexasiloxane (Peak 30) was only observed in the ethyl acetate extract of BKP-I. On the other hand, dioctylbenzenedicarboxylic ester (i.e. dioctylphthalate) (Peak 25) was seen in both the ethyl acetate and cyclohexane extracts of all wood pulps with the exception of the cyclohexane extract of UBKP-I. The same is true for 1,2,-dibenzenedicarboxylic acid diisobutyl ester (Peak 12). When these impurity components are discounted, it is striking how few volatile and detectable components are extracted from both the bleached and unbleached Kraft pulps relative to the CTMP pulps.

It is observed that many more peaks are found in the CTMP-I ethyl acetate extract as compared with the BKP-I ethyl acetate extract, which is in keeping with the fact that per cent extractives of the former is 10 times greater than that of the latter. Vanillin which is basically a degradation product of the lignin from wood, was found in all of the ethyl acetate and cyclohexane extracts with the exception of BKP-I. It was also observed in the water extracts of CTMP-I and CTMP-II. Its oxidation product, vanillic acid, was also found in the ethyl acetate extract of CTMP-I.

Examination of the water extracts via GC/MS (Figs. 8 and 9) indicates that analysis of only the volatile fraction of an extract can be misleading. Even though a much larger amount of the extract was used for injection than with the ethyl acetate extract and bearing in mind the much higher per cent extractives obtained with water, very few different compounds were observed. This is probably due to the fact that the polar compounds extracted have lower vapour pressure and hence GC may not be adequate for their separation.

Compounds designated by peak numbers 40 to 54 were uniquely extracted only by water and should constitute the more polar compounds. In addition, only vanillin and 4-hydroxy-3-methoxybenzeneacetic acid which is freely soluble in hot water were identified in the water extracts. It is likely that either supercritical fluid chromatography or column liquid chromatography could give a clearer picture of the water extracts. Another possibility for our failure to observe in these extracts many components by GC/MS, is that the type of column used may not be adequate for

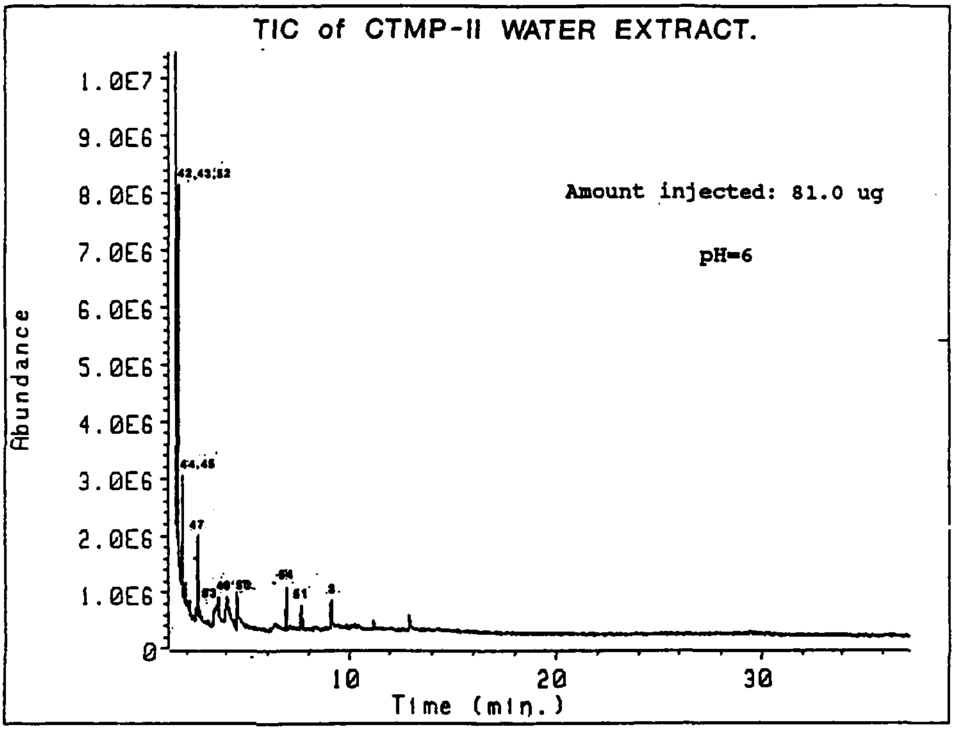

Figure 8 GC/MS of CTMP-II water extract. Conditions same as Figure 6 except 0.5 μl injection.

separating polar compounds. A more polar column and/or a more efficient column may be the answer to this problem.

As would be expected, the least polar compounds were generally extracted by cyclohexane. Of special mention here is dehydroabietic acid. It is a resin acid typically found in pinewoods. Another observation made here is that although the cyclohexane per cent extractives of all the pulps were similar, with the exception of BKP-III, the compounds extracted were different. For example, dehydroabietic acid, methyl 4-methyl-dibenzofuran-1-carboxylate and 1-hexadecanol were only found in UBKP-I and not in the other cyclohexane extracts. Also, vanillin was observed in both the CTMP pulps extracted with cyclohexane as well as in UBKP-I, but not in the BKP-I cyclohexane extract.

Although it was possible in this research to identify a relatively large number of compounds, no chlorinated material was identified in any of the pulp extracts. This could be due to the fact that the chlorinated material is present in trace quantities, which the full scan mode of the mass spectrometer may not detect due to lack of sensitivity. Future work will concentrate on detecting and identifying these chlorinated species using selected ion monitoring, negative ion mass spectroscopy and appropriate chlorinated standards.

In summary, based on the per cent extractives of the pulps studied the results clearly indicate that (a) CTMP pulps yield more water extractives than Kraft pulps,

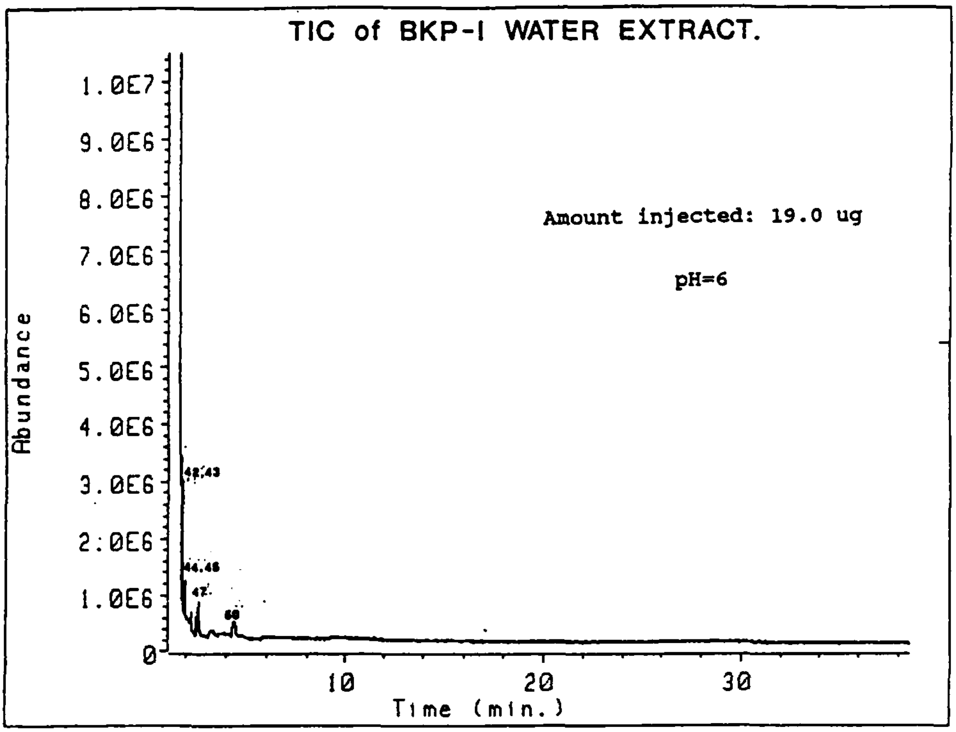

Figure 9 GC/MS if BKP-I water extract. Conditions same as Figure 8.

(b) ethyl acetate and cyclohexane extracts of the two pulp types are generally similar but lower than water extracts and (c) the unbleached Kraft pulp yielded more extractives than the bleached Kraft pulp. In regard to component identification, (a) chlorinated material was not observed in this broad base study; (b) cyclohexane per cent extractives of all the pulps were similar, yet different compounds were extracted and (c) some impurities from handling were incorporated into each extract.

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