A study of polymerization of aspen *(Populus)* wood lipophilic extractives by SEC and Py-GC/MS

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SUMMARY

Studies have been conducted on the formation of polymerised wood resin in model compounds and in lipophilic extracts of aspen. Our studies indicate that polymerization of wood resin components occurs during seasoning of aspen wood. The polymerization probably occurs via oxidation of fatty acids, especially the unsaturated ones, and glyceride components. It results in formation of products that are difficult to dissolve in normal solvents, depending on the extent of the polymerization. Also, the polymerization seems to result in the formation of sterols, compounds that are typically associated with "aspen wax". This implies that the seasoning practices used in aspen mills can result in the formation of polymerized wood resin that will be difficult to remove if present in pulp and paper products. On the other hand, these problems may be minor compared to using unseasoned wood.

KEYWORDS:
Aspen, extractives, polymerization, size exclusion chromatography, Py-GC/MS, wood resin, pyrolysis

INTRODUCTION

Aspen is a particularly resinous wood species *(1)* that sometimes leads to pitch deposition problems in aspen pulp production. The deposition problems are attributed to "aspen wax" and can occur in the brownstock *(2-4)* in the bleach plant *(5)* and on paper machines (6). Consequently, considerable efforts are expended to minimize the amount of residual lipophilic extractives in aspen pulp *(2,3,5,7-10)*. They can include wood or chip seasoning, good barking practices especially in winter when the frozen bark is difficult to remove, addition of tall oil in the digester to improve the saponifiable:unsaponifiable ratio of aspen extractives, maintenance of effective residual alkali in kraft digesters, good brownstock washing, good white liquor clarification, and addition of wetting agents in the washing process. Kraft mills that use an aspen furnish find it advantageous to periodically swing to a softwood furnish as the higher soap content of the softwood wood resin helps to clean out the pitch deposits accumulated on mill equipment from aspen runs.

Despite all the preceding measures, it is difficult to reduce the residual extractives in the bleached pulp to undetectable levels. The residual level of extractives is higher than desirable for some customers. Questions arise as to why there are measurable residual levels of extractives in fully bleached aspen pulps, considering the extensive processing and washing of the pulps. Could this be due to polymerization of wood resin? Are the seasoning conditions conducive to the polymerization? Several reports have indicated that wood resin components, in both softwoods and hardwoods, can polymerize to give products that cause troublesome pitch. For example:

a) Ohtani and co-workers *(11)* studied the polymerization of unsaturated fatty acids and alcohols by conditioning model compounds in an oven at 105 °C. In the compounds studied, namely, oleyl alcohol, oleic acid and linoleic acid, polymerization started to occur after about 3 hours to form polymeric compounds with molar masses that exceeded 6000 Daltons. Beyond 50 hours, the polymerization resulted in compounds that were insoluble in organic solvents. Size exclusion chromatograms of the compounds that formed after 50 hours of conditioning exhibited the same profiles as those of pitch deposits that had occurred in hardwood kraft mills thus confirming the occurrence of polymerized wood resin compounds in the pitch deposits.

b) Raymond and co-workers *(6)* characterized polymeric material in paper machine deposits. Their results indicated that polymerised pitch deposits contained saturated carbon bonds, was composed of approximately 30% chlorine by weight, and had molecular weights that ranged up to 7500 Daltons.

b) Zheng and co-workers *(12)* characterized polymerised glycerides and pitch components by size exclusion chromatography. From their data the authors concluded that polymeric materials in the deposit (from a bleached kraft mill) were mainly polymerised triglycerides and fatty acids. The presence of high molecular weight fatty acids and esters in the deposit suggested that oxidative bleaching may lead to polymerization. A similar analysis of a deposit from a news mill suggested that polymerised fatty acid glycerides and fatty acids were major components in the deposit.

c) Bialczak et al. *(13)* studied changes in the chemistry of extractives during ageing of TMP paper. Their data indicate

that extractives polymerise to such an extent that there was incomplete removal of the extractives by solvent extraction of the paper. Analysis by GC and size exclusion chromatography demonstrated that the chemistry of the extractives changed with ageing to form compounds that were not extractable. However, the chemistry of the polymerized extractives was alluded to but not studied.

The objective of our work was to determine whether or not the current wood procurement practices in an aspen bleached kraft pulp mill, which include a year of seasoning as roundwood and about three weeks as chips, give conditions under which polymerization of some components in the resin occurs to give particularly depositable extractives.

EXPERIMENTAL

The following samples were obtained from the aspen kraft mill: fresh log, seasoned log (one year), and a grab sample of chips from the pile. The logs were debarked, by hand, and then chipped in the laboratory. The chip and bark samples were milled and then freeze-dried before extraction with acetone to ascertain their extractives contents.

POLYMERIZATION STUDIES

The polymerization of aspen extractives was studied by conditioning aliquots of the extracts, in glass cover slips, in an oven at 105 $^{\circ}$C for 24 and 48 hours. An unsaturated fatty acid, linolenic acid, was processed likewise. Solvent soluble and insoluble portions of the samples were subsequently characterized by size exclusion chromatography (SEC), FTIR and pyrolysis-gas chromatography with mass spectrometry detection (Py-GC/MS).

SIZE EXCLUSION CHROMATOGRAPHY

The acetone extracts were characterized by SEC, a technique that separates compounds according to their molecular weights. The extracts were first dissolved in THF, injected, and then separated in SEC columns. Extractives were detected as they exited the columns by a UV detector (254 nm), and the initial concentration was set to obtain a maximum of 0.2 AU. The SEC parameters were as follows:

   Waters 515 HPLC pump
   Waters 486 Tunable Absorbance detector (set at 254 nm)
   Column set: Shodex KF-806L, KF-805L and KF-804L
   Solvent: THF analytical grade (Fisher Scientific)
   Flow rate: 0.7 cm3/min.
   Concentration of the injected solution: 1-3 mg/cm^3
   Injection volume: 50 μL
   Temperature: 55 °C
   Detector: UV at 254 nm.
   Data acquisition: achieved using ASTRA software

The chromatographic columns were calibrated with polystyrene as there are no known standards for polymerized wood resin. After a reconstruction of the distribution, different moments (statistical averages) of the distribution were calculated. These moments are:

   MW_n: Number-average molecular weight
   MW_w: Weight-average molecular weight
   MW_z: Z-average molecular weight

which respectively give more statistical weight to low, medium, or high molecular weight portion of the distribution. The ratios MW_w/MW_n, MW_z/MW_n and MW_z/MW_w represent the polydispersity of the samples. The narrower the distribution, the closer to 1 the polydispersity values are.

Due to the absence of standards to compare the extractives to, the results of the analyses are expressed as polystyrene equivalent; therefore they are not absolute values.

PYROLYSIS-GAS CHROMATOGRAPHY WITH MASS SPECTROMETRY DETECTION

Py/GC/MS is an instrumental method that enables a reproducible characterization of intractable and non-volatile macromolecular compounds. It entails application of thermal energy in a helium atmosphere to produce volatile fragments and products from a macromolecule – compounds capable of being analyzed using GC/MS. It differs from GC/MS in the type of sample analysed and the method by which it is introduced to the GC/MS system. Instead of the direct injection of a highly refined organic solution, a few μg of the original natural material is analysed directly. Thus compounds that are not amenable to analysis by GC and GC/MS are ideal candidates for Py-GC/MS analysis. The analytical conditions were as follows:

PYROLYSER:
   PY-2020 (Frontier Laboratories, Japan) attached to a capillary column)
   Oven temperature: 300 $^{\circ}$C
   Pyrolysis temperature: 450 $^{\circ}$C for 20 s and 650 $^{\circ}$C for 20 s
   Pyrolysis feature: sequential, 450 $^{\circ}$C to detect lower polymeric matter and then 650 $^{\circ}$C to detect recalcitrant polymers
   10-30 μg samples loaded into quartz tubes
   0.5 μL of tetramethyl ammonium hydroxide (25% in methanol) methylating agent were added onto the samples to enable in-situ methylation of the components

GC:
   Varian 3900
   Injection temperature: 300 $^{\circ}$C
   Injection method: 1:25 split
   Column: DB5-HT: 30 m x 0.25 mm i.d. x 0.10 μm film thickness
   Flow rate: 1.6 mL/min
   Temperature programming: 50 $^{\circ}$C for 2 min, 8 $^{\circ}$C/min to 310 $^{\circ}$C, hold for 0.5 min

MS:
   Varian Saturn 2100T ion trap
   Interface temperature: 300 $^{\circ}$C
   Ion trap temperature: 250 $^{\circ}$C
   Electron ionization
   Scan range: m/z 50-650

RESULTS
EXTRACTIVES CONTENT

The data on extractives contents of the samples in Table 1 show that seasoning about 1 year in log form reduced the extractives content by about 60%. The extractives content of the mill chip samples was between that of the fresh log and seasoned logs, indicating that they were partially seasoned. The bark samples contained much more extractives than the wood samples; this illustrates the importance of good barking practices.

MOLECULAR WEIGHT DISTRIBUTIONS

Table 2 summarizes the MW results obtained from the different extractives. Comparing fresh and seasoned chips, and also fresh and seasoned bark, we see that aging results in an increase in the average MW of the extractives. The MW distributions of the extractives of mill chips fell in between those of the fresh and seasoned chips; the mill chips could thus be regarded as moderately aged.

Sample	Extractives content [%]
Chips from fresh log	4.22
Chips from seasoned log	1.70
Mill chips	2.54
Bark from fresh log	32.8
Bark from seasoned log	7.68

Table 1. Acetone extractives content of aspen samples.

These results can also be visualized in Figures 1-2, where the MW distributions (SEC results) are plotted as relative extractive concentration vs. molecular weight, expressed again in PST equivalent. In Figure 1, all the results for chips are plotted. The three profiles have similar peaks, but of different intensities. The fresh chips profile has its highest peak at a lower molecular weight than the highest peak of the seasoned chips profile. The high molecular weight extractives of the seasoned chips have increased at the expense of the low molecular weight extractives. Thus the aging process results in their polymerization, explaining their increase in molecular weight. The mill chips profile displays an in between profile, i.e., no peaks really stand out and there are 2-3 major peaks spread between the low and the high molecular weight regions. All polydispersities are similar. The SEC results comparing fresh bark and seasoned bark are presented in Figure 2. Here, the two profiles are not really similar, and they also show different polydispersities; the seasoned bark profile is broader than the fresh bark one. The fresh bark has two main peaks encompassing most of the extractives, while for the seasoned bark there are 5-6 distinct peaks of similar intensities, and the intensities of the high MW peaks are significantly greater than those for the fresh bark. Nevertheless, a polymerization mechanism is consistent with the difference between the fresh bark profile and the seasoned bark profile.
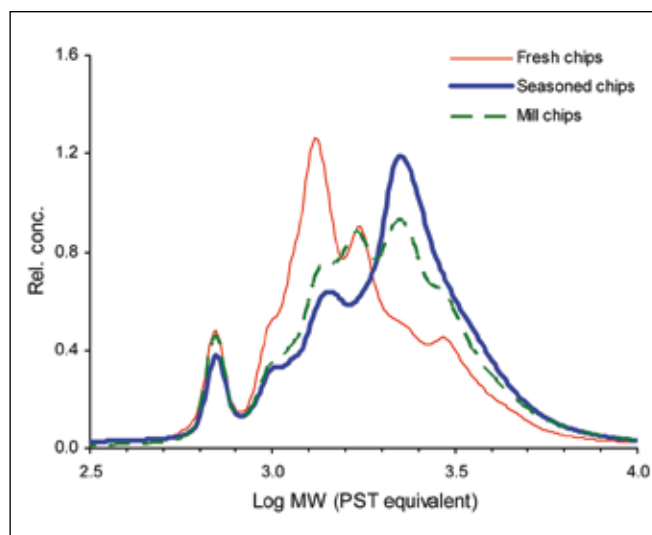

Figure 1. SEC of extractives from fresh and seasoned chips. Results are expressed as relative concentration vs. log MW (PST equivalent).
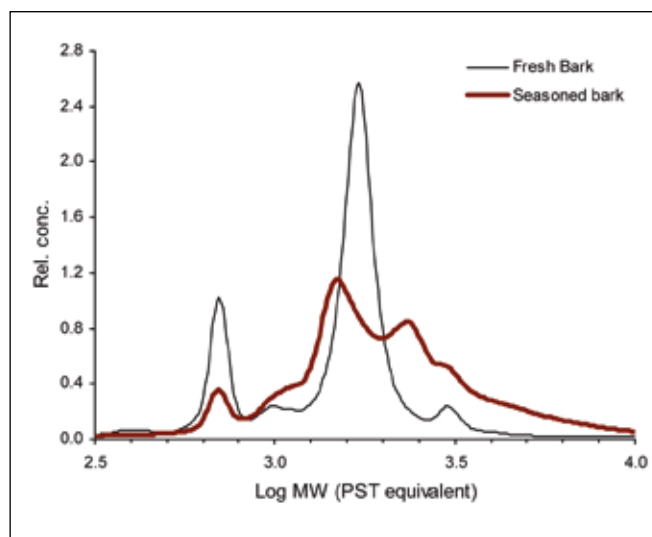

Figure 2. SEC of extractives from fresh and seasoned bark. Results are expressed as relative concentration vs. log MW (PST equivalent).

As seen in Figures 1-2, the seasoned chips and seasoned bark profiles are quite similar, being different mostly in one peak intensity. On the other hand, fresh bark and fresh chips have quite different profiles.

Average MW expressed as polystyrene (PST) equivalent					
Sample	Molecular weight			Polydispersities		
	MW_n	MW_w	MW_z	MW_w/MW_n	MW_z/MW_n	MW_z/MW_w
Fresh chips	1400	1840	2590	1.3	1.9	1.4
Seasoned chips	1690	2270	3030	1.3	1.8	1.3
Mill chips	1590	2150	2960	1.4	1.9	1.4
Fresh bark	1290	1610	2110	1.2	1.6	1.3
Seasoned bark	1610	2230	3230	1.4	2.0	1.4

Table 2. Summaries of the average MWs of the different extractives.

POLYMERIZATION STUDIES
LINOLENIC ACID

Polymerization of linolenic acid showed that the sample became sticky with time and formed a film after 48 hours of conditioning. The film that formed was 100% soluble in dichloromethane solvent after 24 hour conditioning but partially soluble after 48 hours of conditioning. The solubility of the film was assessed in several common laboratory solvents (hot and cold) and it was impossible to completely dissolve it in any of the solvents tested.

Characterization of the samples by FTIR yielded spectra shown in Figures 3 and 4. After polymerization the following observations were made for linolenic acid: the 3011 cm^{-1} absorption band disappeared; the 1712 cm^{-1} absorption band split into a doublet (1711 and 1737 cm^{-1}); peak broadening and loss of resolution occurred in absorption bands below 1410 cm^{-1}; peaks that stand out after polymerization are at 2924, 2854, 1711, 1733, 1462, 1176, 973, 726 cm^{-1}. The main wavelengths in the FTIR functional groups of the linolenic acid are shown in Table 3. The FTIR spectra of the soluble and insoluble portions of polymerized linolenic acid (Figure 4) are similar to that of the polymerized compound, except that the doublet at 1711 and 1737 cm^{-1} occurs only in the soluble fraction and the absorption bands below 1410 cm^{-1} are better resolved than in the original non-extracted polymer. From these observations, it appears that the appearance of a doublet at 1711 and 1737 cm^{-1} might possibly be used to indicate the presence of polymerized wood resin in the extracts.
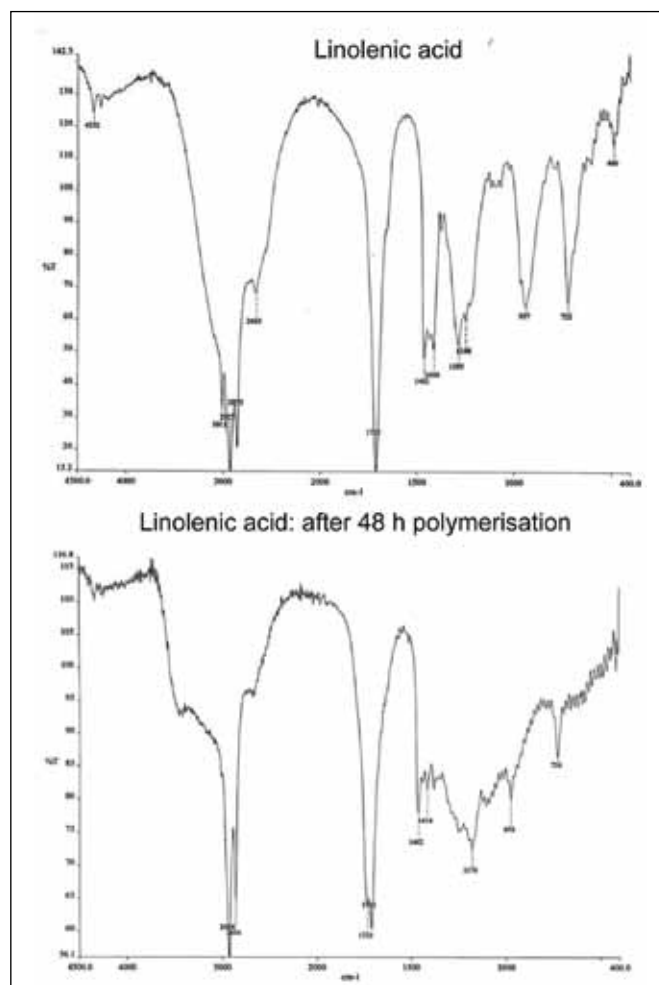
Figure 3. FTIR spectra of polymerised and non polymerised linolenic acid.
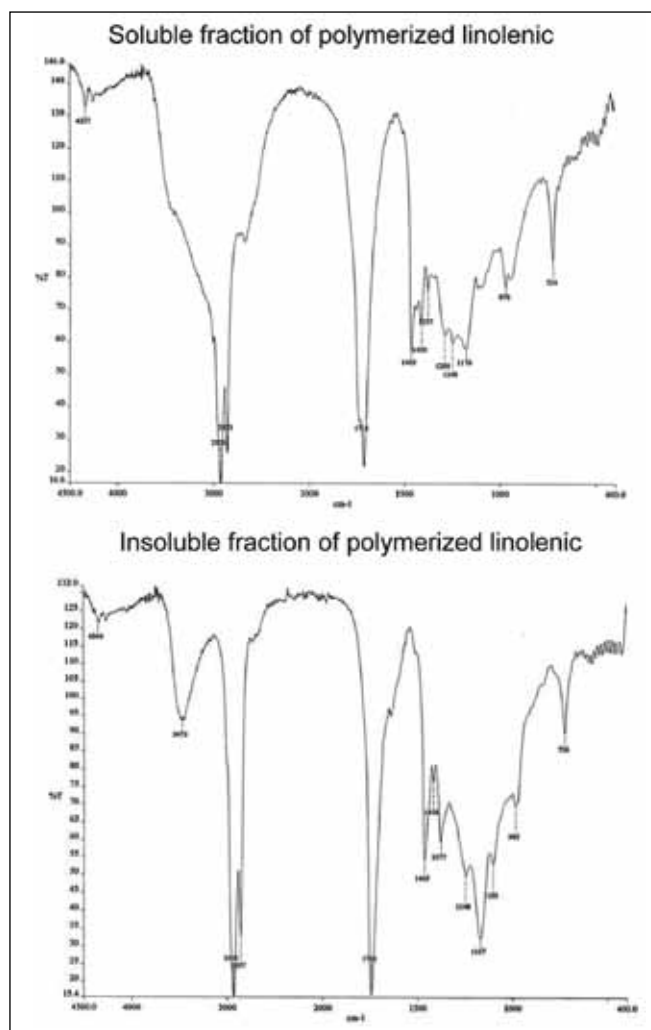
**Figure 4.** FTIR spectra of the soluble and insoluble fractions of polymerized linoleic acid.

Wavelength [cm^{-1}]	Functional group
3011	CH stretching of cis double bond (=CH)
2924, 2854	Symmetric and asymmetric stretching vibrations of aliphatic
1711	CH$_2$ groups
1462	C=O stretching vibration (carboxylic acid)
1410	Bending vibration of CH$_2$ and CH$_3$ aliphatic groups
1176	Rocking vibration of CH$_2$ and CH$_3$ aliphatic groups
949, 988	Stretching vibration of C-O ester groups
993	Cis trans doublet Trans trans singlet

Table 3. The main wavelengths in the FTIR functional groups of linolenic acid.

Results of studies on polymerization of extracts of fresh aspen mimicked those of the linolenic acid in that the extractives became tacky as the polymerization progressed. The polymerised material was soluble after 24-hour conditioning and partially soluble (14%) after 48-hour conditioning. The solubility behaviour of the polymeric film was the same as that of polymerised linolenic acid.

The FTIR spectra of the polymerised sample are displayed in Figure 5. Overall, the changes in spectral pattern upon polymerization mimic those of linolenic acid, e.g., the appearance of a doublet at 1711 and 1737 cm^{-1}.
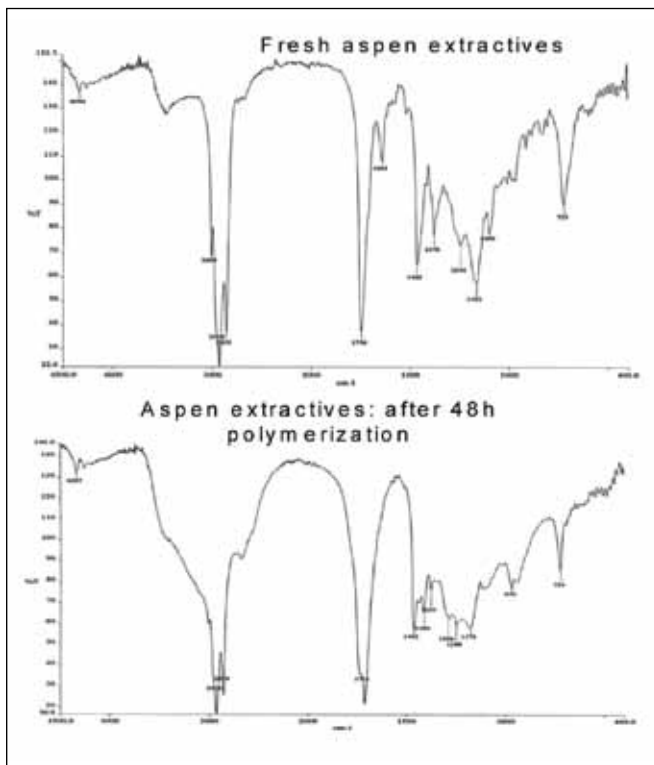

Figure 5. FTIR spectra of polymerised and non-polymerised fresh aspen extractives

Molecular weight distribution data of the polymerised matter are shown in Table 4 and in Figure 6. The figure shows that polymerization significantly broadens the elution profile; what was mainly a single narrow peak at time 0 became a wide convolution of peaks, with a large portion extending towards higher molecular weights. As a result, average MW's and polydispersities of the extracts increased when exposed to high temperatures. The data show that the polymerization is quite extensive, especially in the DCM extracts of the polymeric matter. The values are much higher than that of seasoned wood (values in Table 4). This is not surprising as it should be expected that seasoning in an oven would induce more rapid and drastic seasoning than outside wood storage.

Sample	MW_n	MW_w	MW_z	MW_w/MW_n	MW_z/MW_n	MW_z/MW_n
Extracts of aspen at time 0	1470	1560	1630	1.1	1.1	1.0
DCM extracts at time 0	1460	1550	1620	1.1	1.1	1.0
Extracts of aspen after 48 h	1120	1780	3450	1.6	3.1	1.9
DCM extracts after 48 h	1500	2950	7170	2.0	4.8	2.4

Table 4. Effect of polymerisation on molecular weight distribution of extracts of fresh aspen.
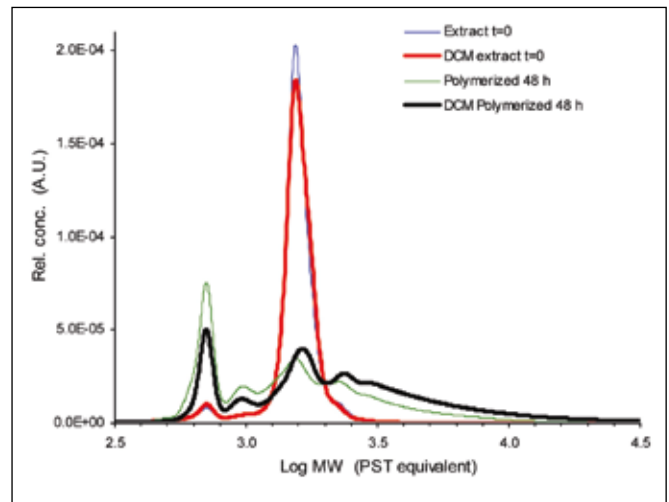
Figure 6. SEC of extracts of polymerised and non-polymerised aspen extracts. Results are expressed as relative concentration vs. log MW (PST equivalent)

PY-GC/MS ANALYSES

The polymerised extracts were characterized by Py-GC/MS. This technique has previously been used for quantitative determination of organic compounds in various matrices *(14-16)*.

24-H POLYMERIZATION

Pyrograms of the original extracts and the soluble and insoluble portions of the polymerised extracts are shown in Figure 7. The data show that:

1. The saturated fatty acids decrease upon polymerization.
2. The unsaturated fatty acids decrease upon polymerization; they are present in lower amounts in the soluble fraction and completely absent in the insoluble fraction.
3. New compounds, viz., nonanedioic and octanedioic acids, are present in the soluble and insoluble fractions of the polymerized matter.
4. The presence of peaks that elute at high retentions times (beyond 20 minutes) are evidence for the formation of higher molecular weight fatty acids.
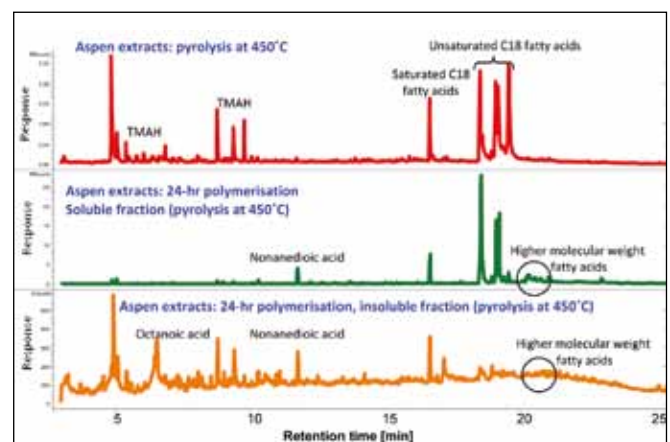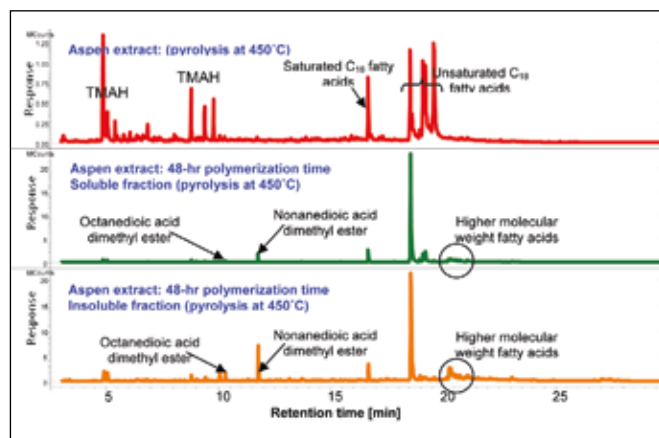

Figure 7. Pyrograms of polymerised and non-polymerised aspen extracts after conditioning for 24 hours.

48-H POLYMERIZATION

Pyrograms generated by 48 hour pyrolysis shown in Figure 8, indicate the following:

1. The dioic acids are present in both the soluble and insoluble fractions of the polymerized extracts, albeit in higher amounts in the insoluble fraction.
2. There is a significant decrease in the amounts of the saturated and most of the unsaturated fatty acids in the polymerized fractions, more so in the insoluble fraction.
3. The insoluble fraction of the polymerized extracts displays evidence of higher amounts of high molecular weight fatty acids than the soluble fraction.

Figure 8. Pyrograms of polymerised and non-polymerised aspen extracts after conditioning for 48 hours.

Pyrolysis at 650 °C shows that the components remaining after initial pyrolysis at 450 °C are mainly sterol type compounds as shown in Figure 9. The amounts of sterols increase significantly after polymerization. Identification of the sterols via the NIST mass spectral library database indicated the presence of sterol acetates. The mechanism for the survival or formation of these compounds in the polymeric matrix is not clear.
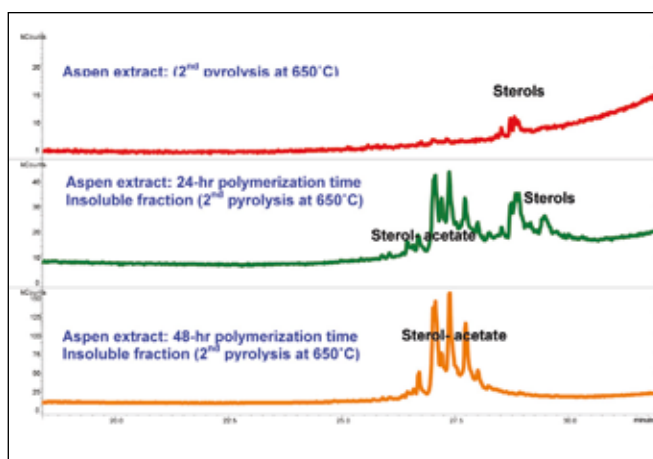
Figure 9. Pyrograms obtained after pyrolysis at a higher temperature show the presence of sterols in the extracts.

DISCUSSION

A severe limitation of SEC is that it requires extraction of the polymeric wood resin from the wood, pulp, or pitch deposit. Once the degree of polymerization surpasses a certain point (e.g., a dozen triglyceride molecules or MW >10,000), the solubility of the polymerized material drops to zero. Thus SEC of polymeric wood resin may very well be looking at only the "tip of the iceberg" – much of the time most of the polymeric material remains un-dissolved in the original sample matrix and MW distributions are determined only of the lower MW fraction that is solvent-soluble.

Py-GC/MS is best suited for characterization of the insoluble polymerised wood resin. For soluble polymerised resin, LC/MS may be the technique of choice as, unlike GC/MS, it is well suited for handling non-volatile and higher molecular weight compounds.

CONCLUSIONS

Our studies indicate that polymerization of wood resin components occurs during seasoning of aspen wood. The polymerization probably occurs via oxidation of fatty acids, especially the unsaturated ones, and glyceride components. The polymerization results in formation of products that are difficult to dissolve in normal solvents, depending on the extent of the polymerization. Also, the polymerization seems to result in the formation of sterol-like compounds, compounds that are typically associated with "aspen wax". This implies that the seasoning practices used in aspen mills can result in the formation of polymerized wood resin that will be difficult to remove if present in pulp and paper products. On the other hand, these problems may be minor compared to using unseasoned wood.

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