Pectic acids in the production of wood-containing paper

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ABSTRACT

The paper reviews recent studies concerning pectic acids or polygalacturonic acids in suspensions of mechanical pulps produced from Norway spruce. Pectic acids dissolve from fibers to an aqueous phase in alkaline conditions such as alkaline peroxide bleaching. They have a low molar mass and a high negative charge density. Pectic acids can have manifold effects on papermaking including reacting with cationic polyelectrolytes and Ca^{2+} ions.

Application:
Interactions of pectic acids with cationic polyelectrolytes can make cationic additives less effective. The precipitation of pectic acids with calcium can cause co-aggregation of colloidal substances.

PECTIC SUBSTANCES ARE IONIC polysaccharides found in the intercellular regions and the cell walls of all higher plants *(1)*. The predominant structural subunit in pectic substances is D-galacturonic acid *(2, 3)* with some minor amounts of neutral sugar units such as D-galactose, L-arabinose, and L-rhamnose. Pectic substances containing no or very few methyl ester groups have the common designation of pectic acids or pectates in their salt forms *(1)*. Pectic substances have wide use as thickening and gelling agents in food technology *(4)*.

The content of pectic substances in Norway spruce is reportedly less than 1% *(5, 6)*. They occur primarily in the middle lamellae and the tori of bordered-pit membranes *(7–10)*. Most pectic substances in Norway spruce wood are methyl-esterified *(10)*. Since they are selective chelators of Ca^{2+} ions, the pectic substances may play an important role in the lignification of wood cells *(6)*.

In the Nordic countries, the predominant raw material for the production of wood-containing paper such as newsprint magazine papers is Norway spruce (*Picea abies*). This review summarizes the chemical properties of pectic substances dissolved from Norway spruce thermomechanical pulp (TMP) and presents some effects of dissolved pectic acids on the production of wood-containing paper.

EXPERIMENTAL

Material and methods

TMP came from a paper mill in southern Finland performing two stage refining of Norway spruce. The pulp consistency was approximately 40%. Pulp storage was at –24°C until use. All the experiments used this pulp except dissolved air flotation. That case used a water sample from a groundwood plant at a board mill in eastern Finland using peroxide bleaching.

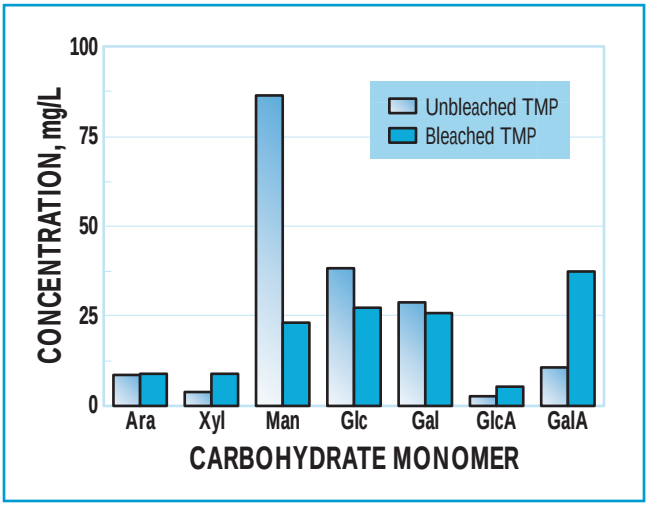
Sampling of DCS. The TMP sample was diluted to 1% consistency with distilled water. The suspension was agitated at 150 min^{-1} at 60°C for 3 h. To remove fibers and other noncolloidal particulate matter, the TMP suspension was centrifuged at 500 g for 30 min. followed by pipetting of the supernatant—the dissolved and colloidal substances (DCS) sample *(11–16)*.

Peroxide bleaching. Portions of TMP were manually mixed with bleaching chemicals in polyethylene bags, diluted to approximately 10% consistency with distilled water, and held at 60°C for 90 min. The samples were then acidified in the bag to pH 5 with SO_2-water. The bag contents were transferred to 3 L glass beakers, diluted to 1% consistency with distilled water, and agitated at 150 min^{-1} and 60°C for 3 h *(11)*.

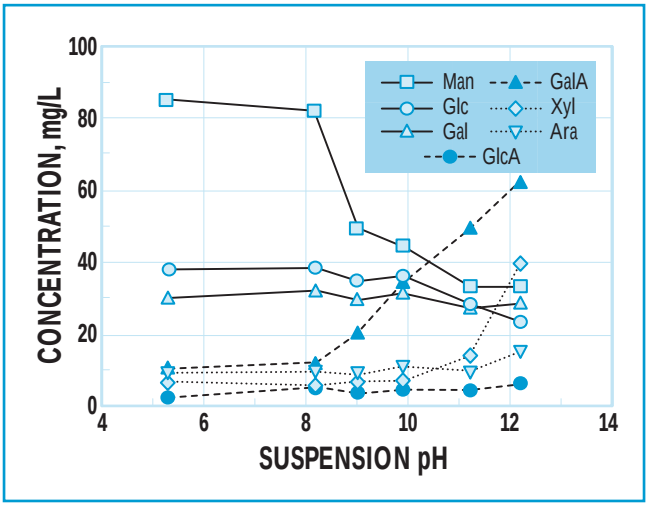
Addition of $CaCl_2$ or poly-DADMAC. Under constant agitation with a magnetic stirrer, analytical grade $CaCl_2$ was added to the DCS samples at 60°C. After agitation at 60°C for 15 min., the samples were centrifuged at 500 g for 30 min. followed by pipetting of the supernatants for analysis *(15, 16)*. Similarly, poly-DADMAC, a low- molar-mass polymer with a high cationic charge density, was added to suspensions of TMP containing fibers and DCS *(13)*.

Isolation of pectic acids

The isolation procedure came from several sources *(2, 17)*. TMP was extracted with n-hexane to remove lipophilic extractives. The resin-free TMP was then suspended in distilled water at 2% consistency. The suspension was agitated with a blade propeller at 200 min^{-1} and 60°C for 3 h. The pH was adjusted to 11 with 1 *M* NaOH several times during the agitation. The suspension was then centrifuged at 500 g for 10 min, and the supernatant was collected. The remaining fiber phase was filtered on a paper filter to collect as much aqueous phase as possible. TMP was again added to the aqueous phase to 2% consistency. The suspension was agitated, centrifuged, and filtered as described above. The aqueous phase was collected, and the pH was adjusted to 7.



1. Pectic acids dissolve from the fibers in alkaline peroxide bleaching (12)



2. Alkaline conditions cause the dissolution of pectic acids from TMP (22)

Component	%
Arabinose	2.1
Xylose	0.8
Rhamnose	1.1
Mannose	1.2
Glucose	1.5
Galactose	5.5
4-O-Me-Glucuronic acid	0.7
Glucuronic acid	0.5
Galacturonic acid	86.6
Total	100.0

I. The relative sugar composition of pectic acids dissolved from peroxide-bleached mechanical pulp

The aqueous phase was then filtered through a Whatman Polycap 75 AS filter with a 0.2 µm pore size to remove colloidal substances. Then 30 mM $CaCl_2$ were added to the filtered sample that was allowed to stand overnight. The sample was then centrifuged at 500 g for 30 min., and the supernatant was removed. The precipitate was washed twice with 30 mM $CaCl_2$ in distilled water. The sample was allowed to stand at least 1 h before each centrifugation to ensure complete precipitation of pectic acids. After this, the precipitate was washed three times with 0.05 *M* HCl in ethanol and three times with ethanol. The precipitate was dried in a stream of nitrogen after the last centrifugation.

The precipitate was dissolved in distilled water, and pH was adjusted to approximately 11 to convert the pectic acids to their sodium salts. The sample was then filtered on a paper filter MN 640D to remove some particles and dialyzed with a Spectra/Por Membrane—mol. wt. cut off 1,000 according to the supplier—to remove salts.

To remove residual calcium, cation exchange was performed with an Amberlite 200 resin. The resin was cleaned and washed according to Sjostrom *(18)*. The resin was regenerated with 5 bed volumes of 2 *M* HCl, washed with 0.5 *M* NaCl until the pH of the effluent was neutral, and rinsed until the conductivity of the effluent was approximately 2 µS/cm. Approximately 25 mg of pectins dissolved in water were added to a 10 mL column. The effluent was collected and again added on the column. The effluent was then collected, dialyzed, and freeze-dried.

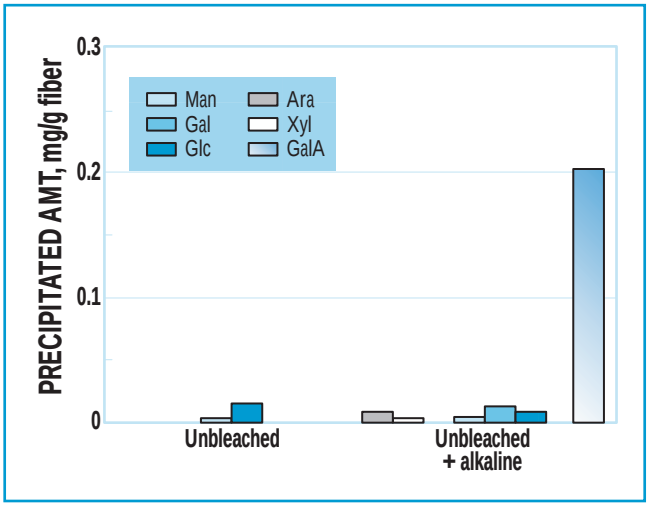
Analyses

Total organic carbon. Total organic carbon (TOC) was determined with a TOC 5050 instrument (Shimadzu Corp., Japan).

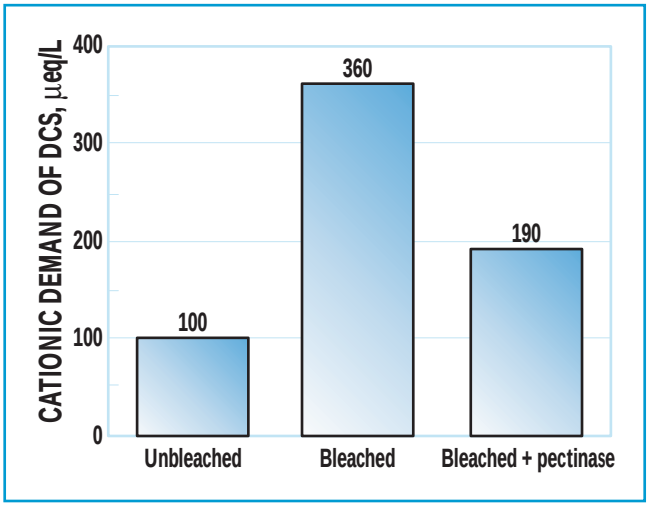
Carbohydrates. Carbohydrates were determined using methanolysis to obtain monomeric methyl glycosides of neutral sugar units and methyl ester methyl glycosides of uronic acids. After being silylated, the monomers were determined by gas chromatography *(19)*. The monomers quantified were arabinose (Ara), xylose (Xyl), mannose (Man), glucose (Glc), galactose (Gal), glucuronic acid (GlcA), and galacturonic acid (GalA). In some analyses, rhamnose (Rha) was also determined.

Lipophilic extractives. These materials were determined by a recently developed method using extraction with methyl tert-butyl ether (MTBE) and analysis by gas chromatography *(20)*.

Cationic demand and charge density. Determination of these properties used a Rank Brothers Charge-Analyser II (Rank Brothers Ltd., England). The instrument uses streaming current detection for end-point determination. Polybrene and



3. After alkaline treatment of the dissolved substances released from unbleached TMP (Unbl+alk), some pectic acids could be precipitated with $CaCl_2$



4. Alkaline peroxide bleaching causes an increase in the cationic demand of the DCS released from the fibers, and enzymatic degradation of pectic acids results in a considerable decrease in the cationic demand (31)

potassium polyvinyl sulfate (PVSK) were used as standard polymers.

Turbidity. Measurement of turbidity expressed as Formazin Turbidity Units (FTU) was measured with a Hach DR/2000 instrument (Hach Co., USA).

RESULTS AND DISCUSSION

The dissolution of pectic acids from TMP

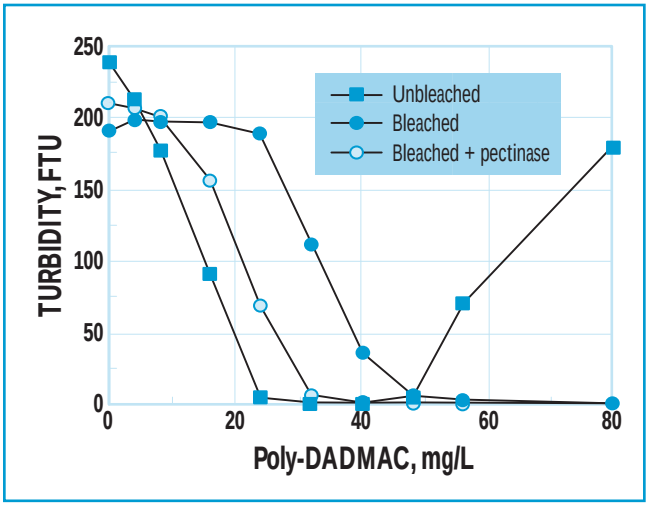
Pectic acids dissolve from TMP fibers in alkaline peroxide bleaching. The large amounts of galacturonic acid obtained by methanolysis in a sample of DCS from peroxide-bleached TMP compared with that of unbleached material indicate this. **Figure 1** *(11, 21)* shows the concentrations of carbohydrate monomer. Only trace amounts of the galacturonic acid units occur in mono- and disaccharide analyses. This suggests that the galacturonic acid units detected after methanolysis are constituents of oligo- or polysaccharides. The alkaline conditions primarily cause the dissolution of pectic acids in peroxide bleaching *(11, 22)* as **Fig. 2** shows. Results in the figure are for TMP suspensions agitated at 60°C for 3 h followed by neutralization and centrifugation. β-elim- ination reactions that occur in parallel with demethylation can degrade methylated pectic substances *(2)*. The initial dissolution of pectic acids at pH above 8 suggests that their dissolution somehow relates to demethylation. As a rule, the solubility of pectins in acidic water decreases as the carboxylic acid content increases, i.e., when the degree of esterification decreases *(1)*. Converting the carboxyl groups to their soluble salt forms (monovalent cations) can overcome the decreased solubility. In alkaline peroxide bleaching, addition of sodium uses sodium hydroxide and sodium silicate. The pH of normal papermaking operations is 4–8. Pectic acids are substantially ionized at pH 5 *(23)*. This means they are usually very soluble in paper machine circulation waters. The mechanism behind the dissolution of pectic acids from pulp fibers is still uncertain and requires clarification.

Properties of pectic acids dissolved from TMP

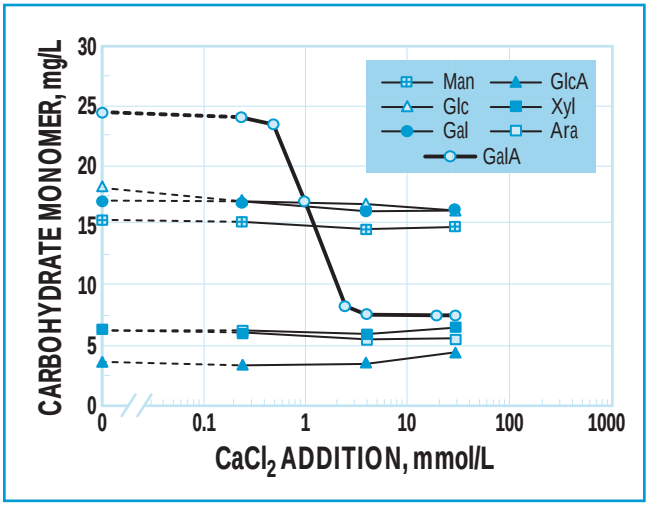
The pectic substances isolated by Ca^{2+} precipitation from the aqueous phase of a suspension of peroxide-bleached TMP consisted primarily of the galacturonic acid units indicated in **Table I**. This is typical for pectic acids *(2, 3)*. The charge density of the isolated fraction of pectic acids was approximately 4.6 meq/g suggesting a very low methyl ester content. The theoretical charge density of pectic acids in their sodium salt form is approximately 5.1 meq/g.

The molar mass of the dissolved pectic acids was approximately 12, 000 as determined by high performance liquid chromatography. This corresponds to a degree of polymerization (DP) less than 100 and suggests that the dissolved pectic acids are cleavage products of larger pectin molecules in the wood tissue. The molar mass of pectic acids isolated from a mill sample was lower at approximately 3500. This corresponds to a DP of 20–25 *(16)*. By acid hydrolysis of pectin, Powell *et al. (24)* obtained pectic acids of similar chain length that they suggested were because uninterrupted polygalacturonate chain sequences have a narrow distribution of lengths in the native polymer. This is true for many different plants *(24)*.

The narrow molar mass distribution of the pectic acids isolated in this study may also have resulted



5. Compared to suspensions of unbleached TMP, much more cationic polymer is required for effective aggregation of colloidal substances in suspensions of peroxide-bleached TMP (Unbl = Unbleached, Bl = Peroxide-bleached, B1+Pect = Peroxide-bleached and pectinase-treated) (13)



6. Upon addition of $CaCl_2$ to DCS released from peroxide-bleached TMP, pectic acids are precipitated (here shown by the decrease in galacturonic acids) (15)

from the isolation procedure, since a certain molar mass of pectic acids is necessary for intermolecular complex formation with Ca^{2+} ions *(25)*. Addition of $CaCl_2$ to water samples or filtrates from peroxide bleached mechanical pulp causes substantial precipitation of pectic acids *(15, 16, 26, 27)*. One could therefore assume that the isolate obtained represents pectic acids present in suspensions of peroxide bleached mechanical pulps. The fact that acid treatment at pH 2 for 1 h at room temperature did not further degrade the pectic acids with a molecular weight of 12,000 supports this.

Only small amounts of pectic acids dissolve from unbleached mechanical pulp. Some carbohydrates containing galacturonic acid units—approximately 1 kg/ton—occur in suspensions of unbleached mechanical pulps *(11, 15, 16)*. If these carbohydrates were building blocks of pectins, they would most probably be very low molecular weight or methylated to a degree, since Ca^{2+} ions could not precipitate them as **Fig. 3** shows. Some precipitation occurred after an alkaline treatment that causes demethylation and exposes the carboxylic groups. Approximately one-third of the total amount of galacturonic acid units was precipitated with $Ca\ Cl_2$ after the alkaline treatment of a water sample from unbleached mechanical pulp. The precipitate obtained by $CaCl_2$ addition to the alkali treated sample consists primarily of galacturonic acid as Fig. 3 shows. This suggests that most galacturonic acid-containing polysaccharides found in the aqueous phase in suspensions of unbleached mechanical pulp are methylated building blocks of pectins.

KEYWORDS
Agglomeration, calcium, cationic compounds, colloids, extractives, flocculation, mechanical pulps, pectic acid, peroxide bleaching, picea abies, polysaccharides, wood resin.

Possible effects of pectic acids on papermaking

Interactions with cationic polymers. Polyelectrolyte titration commonly determines the amount of anionic material in paper mill circulation waters and evaluates polyelectrolytes *(28–30)*. For mill water samples, the value obtained from the titration can be expressed as the cationic demand in meq/L.

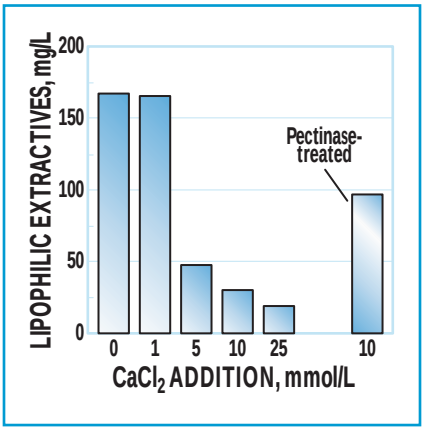
Alkaline peroxide bleaching causes the three- to four-fold increase in the cationic demand of DCS released from TMP seen in **Fig. 4** for samples representing an open water circulation system *(31)*. Enzymatic degradation of pectic acids results in a considerable decrease in the cationic demand *(31)*. Approximately half the cationic demand of DCS from peroxide bleached TMP—approximately two-thirds of the increase compared with unbleached TMP—is the result of the dissolution of pectic acids as Fig. 4 shows. Enzymatic depolymerization of pectic acids that resulted in a substantial decrease in the cationic demand of the DCS released from peroxide-bleached TMP of Fig. 4 showed this *(31)*. After degradation, the constituents of pectic substances can no longer form polyelectrolyte complexes with the oppositely charged polymer. Such DP-dependent complexing also occurs with cationic polyethyleneimine and synthetic anionic polymers *(32, 33)*.

Similar to the above observations, the amount of cationic polymer necessary to aggregate colloidal substances—primarily wood resin—in a suspension of peroxide bleached TMP can be higher than the amount needed in an unbleached suspension as **Fig. 5** shows *(13, 14)*. Much difference is the result of interactions between pectic acids and the cationic polymer *(13)*. The pectic acids are largely responsible for the increased polymer dose needed in the peroxide bleached suspension. The much lower polymer dose needed for effective aggregation of colloidal substances after enzymatic depolymerization of the pectic acids in the peroxide bleached suspension shown in Fig. 5 indicates this *(13)*. Although quantitatively representing only approximately 5% of the TOC in water samples from peroxide-bleached TMP, the pectic acids are a key factor for anionic material consuming cationic papermaking additives *(13, 31)*.

Interactions with Ca^{2+} ions. On addition of $CaCl_2$ to a sample of DCS from peroxide-bleached TMP, pectic acids precipitate to a great extent *(15, 16)*. **Figure 6** indicates a decrease in galacturonic acid obtained by methanolysis at increasing concentrations of $CaCl_2$. The precipitation of pectic acids is accompanied by aggregation of colloidal wood resin (not shown) *(15)*. A mechanism commonly suggested for the interactions between calcium and polygalacturonic acid carboxyl groups has been described by an "egg-box" model *(24, 34, 35)*. This is a two-stage process consisting of an initial dimerization and subsequent aggregation of these pre-formed "egg-boxes."

The aggregation of colloidal wood resin droplets accompanies the precipitation of pectic acids *(15, 16, 26, 27)*. Colloidal wood resin in suspensions of unbleached mechanical pulp is not very susceptible to electrolyte-induced aggregation *(15, 16, 26, 36, 37)*. With added pectic acids, calcium ions can cause extensive aggregation of colloidal wood resin in suspensions of unbleached mechanical pulp. Calcium ions and pectic acids can act as a two component flocculation system to aggregate the colloidal wood resin. Calcium ions with alginate substances closely related to pectic acids can effectively flocculate microcrystalline cellulose *(38)*.

If the calcium ion with pectic acid-induced aggregation of wood resin has no control, it may cause undesirable effects in the papermaking process. It can also benefit the papermaking process stages where aggregation is necessary, such as water clarification by sedimentation or dissolved air flotation. Wood resin is therefore effectively removed in dissolved air flotation upon the addition of calcium ions to a mill filtrate from peroxide-bleached pulp containing pectic acids as **Fig. 7** shows *(27)*. The precipitation of pectic acids may also cause a substantial decrease in the cationic demand *(27)*. The decrease has the same order of magnitude as that obtained by enzymatic depolymerization of the pectic acids. This also shows that pectic acids are a major factor contributing to the cationic demand in a very closed water circulation system.



7. Lipophilic extractives or wood resin are effectively removed in dissolved air flotation with $CaCl_2$ due to the presence of pectic acids (27)

CONCLUSION

Pectic acids are dissolved in peroxide bleaching of mechanical pulp from Norway spruce. Their main monomeric constituent is galacturonic acid. The molar mass of the pectic acids dissolved is approximately 12,000 D. This corresponds to a mean DP of less than 100. The charge density is approximately 4.6 meq/g at neutral pH indicating a very low methyl ester content.

Little or no pectic acids dissolve from unbleached mechanical pulp. The small amounts of pectic substances dissolved from unbleached pulp consist primarily of methyl-esterified pectins.

Pectic acids can cause a substantial increase in the cationic demand in water samples from mechanical pulps. They may also render cationic papermaking additives less effective.

Ca^{2+} ions that can cause co-aggregation of colloidal wood resin can precipitate pectic acids. If uncontrolled, this aggregation may give undesired effects in the papermaking process. It can also be beneficial in process stages where aggregation of colloidal substances is necessary such as water clarification by dissolved air flotation. TJ

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