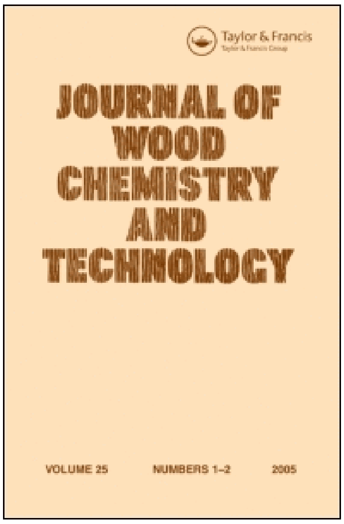

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Chemical Changes in Thermomechanical Pulp at Alkaline Conditions

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ABSTRACT

Chemical changes in thermomechanical pulp (TMP) from Norway spruce at alkaline conditions were examined at pH levels 9, 10, and 11, and temperatures of 40, 50, and 60°C. Alkali treatments were also made in the presence of hydrogen peroxide. The anionic charge of the fibres increased rapidly, following the kinetics of ester bond cleavage. Already at pH 9 and 60°C, acetic acid, methanol, pectic acids, and some lignin material were dissolved. Dissolution of xylans required

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higher pH. Lignin and xylans slowly leached into the water without affecting fibre charge. Leaching caused substantial material loss during extended alkali treatment. At pH 11, hydrogen peroxide almost doubled the overall loss of wood material compared with alkali only. This was partly due to acceleration of the dissolution of xylans and lignin material, but also due to considerable formation of low-molar-mass oxidation products. The effect of hydrogen peroxide on fibre charge was considerable also during extended treatment.

INTRODUCTION

Mechanical pulping represents about 30% of all pulp production.[1] Intensive research is continuously focused on the properties of mechanical pulp fibres, which are very dependent on the process conditions in pulping and bleaching. Today, there is urgent need to minimise material loss, reduce chemical and water consumption, which are of both economical and ecological importance.

In the Nordic countries, mechanical pulp is mainly produced from Norway spruce, either by grinding or refining. Some wood material loss occurs already during pulp production, even without the use of chemicals, and so-called dissolved and colloidal substances (DCS) are readily released from the wood tissue into the process water.[2–4]

The composition of DCS is now well known and DCS include hemicelluloses, lipophilic and hydrophilic extractives, lignin and lignin-related substances.[2,3] In closed water systems of integrated pulp and paper mills, the DCS may accumulate to high concentrations and cause various detrimental effects on papermaking,[4,5] especially by interacting with added paper chemicals.

It is known that mechanical pulping results in considerable fibre damage, but causes only small chemical changes in the wood material. The chemical changes in wood fibres and the dissolution of wood material are much more substantial when the processes involve chemical treatments, such as in chemi–mechanical pulping, de-inking processes, and peroxide bleaching.

Sodium hydroxide is not only used in chemi–mechanical pulping, but is essential also in peroxide bleaching and de-inking. Thus, a better understanding of alkali-induced alteration of TMP fibres and clarification of the effects of hydrogen peroxide are important issues.

It is generally assumed that alkaline bleaching of TMP with hydrogen peroxide causes oxidative degradation of wood substances, which in its turn results in increased negative charge of the fibres.[3,5] However, the charge increase can also be due to alkali-induced hydrolysis of naturally occurring ester bonds in carbohydrates and lignin–carbohydrate complexes.[6–8] On the other hand, the combined effect of alkali/peroxide is drastic for the dissolution of fibre material. It has been shown that large amounts of acetic acid (ca. 20 kg/ton), lignin and lignin-related substances, as well as pectic substances and carbohydrates are released into the water phase in alkaline peroxide bleaching.[2,3] The effects of DCS on papermaking and paper quality vary. Some component groups account for decreased efficiency of cationic paper chemicals (e.g., pectins), whereas others influence paper properties negatively (generally extractives and, probably, lignin), or positively (generally hemicelluloses). The overall loss of organic substances during peroxide bleaching of TMP from Norway spruce is about 40 kg/ton.[3,9]

Dissolved galactoglucomannans undergo deacetylation, which leads to their re-adsorption onto fibres.[3] Deacetylation of the galactoglucomannans may also lead to aggregation of colloidal wood resin.[4]

Carboxylic groups are key functional groups in papermaking. They are ionized already at conventional papermaking conditions (pH 5–7.5),[10,11] thereby facilitating swelling of fibres in pulp suspensions and improvement of paper strength. Thus, an increase of the anionic charge in fibres is normally a beneficial effect of peroxide bleaching. Nevertheless, extensive oxidation of wood fibres during peroxide bleaching is not desired, since it can lead to increased consumption of chemicals and decreased pulp yield. In order to get a deeper understanding of mechanical pulp chemistry, it is necessary to distinguish between alkali-induced and peroxide-induced effects.

The objective of the research presented in this article was to obtain a comprehensive description, via a systematic kinetic study, of chemical changes in mechanical pulp fibres during alkaline treatment with and without the presence of hydrogen peroxide.

RESULTS AND DISCUSSION

Although the thermomechanical pulp fibres used were thoroughly pre-extracted and washed, fairly mild alkali treatments released substantial amounts of organic substances into water. Substances released consisted mainly of acetic acid, methanol, hemicelluloses, pectins, and low-molar mass lignin.

Release of Acetic Acid and Methanol

Acetic acid was the most abundant compound released into the water from alkaline treatments of TMP (TMP water). It is formed by alkali-induced ester hydrolysis of the acetyl groups at the C2 and C3 positions of the sugar units in the *O*-acetyl-galactoglucomannan backbone.[12]

Significant release of acetic acid occurred only at pH levels higher than 9 (Fig. 1). At pH 9, the rates were still quite slow even at 60°C. The deacetylation rates were much higher at pH 10 and increased further at pH 11. The release of acetic acid into the water phase was complete after 60 min at pH 11 (60°C).

Addition of hydrogen peroxide did not affect the total release of acetic acid, but influenced the deacetylation rate. Deacetylation was faster in the presence of hydrogen peroxide, being complete after 30 min of treatment at pH 11 and 60°C.

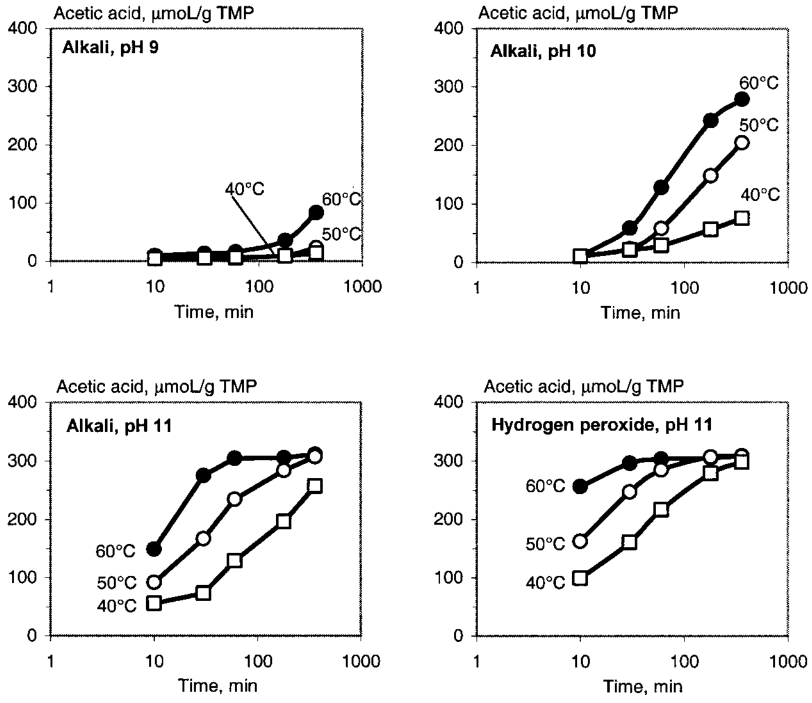

Figure 1. Release of acetic acid from TMP during alkali treatment, with and without hydrogen peroxide, at different temperatures and pH levels.

Release of methanol occurred at mild alkaline conditions (Fig. 2). Methanol formation can be related to cleavage of methyl ester bonds. It is well established that methyl ester bonds are typical for natively occurring polygalacturonic acid, which is the main pectin in spruce wood.[13,14]

The rates of methanol release (Fig. 2) were similar to the rates of acetic acid release (Fig. 1). Already an extended (6 h) treatment at 60°C and pH 9 resulted in a substantial methanol release. Methanol release was dependent on both temperature and pH. After 1 h at pH 11 and 60°C the process was complete and levelled off at 60 μmol/g TMP. This corresponds to a degree of methylation of galacturonic acid units in washed TMP of about 75%.

The presence of hydrogen peroxide resulted in higher amounts of liberated methanol, reaching 80 μmol/g TMP after 1 h of treatment.

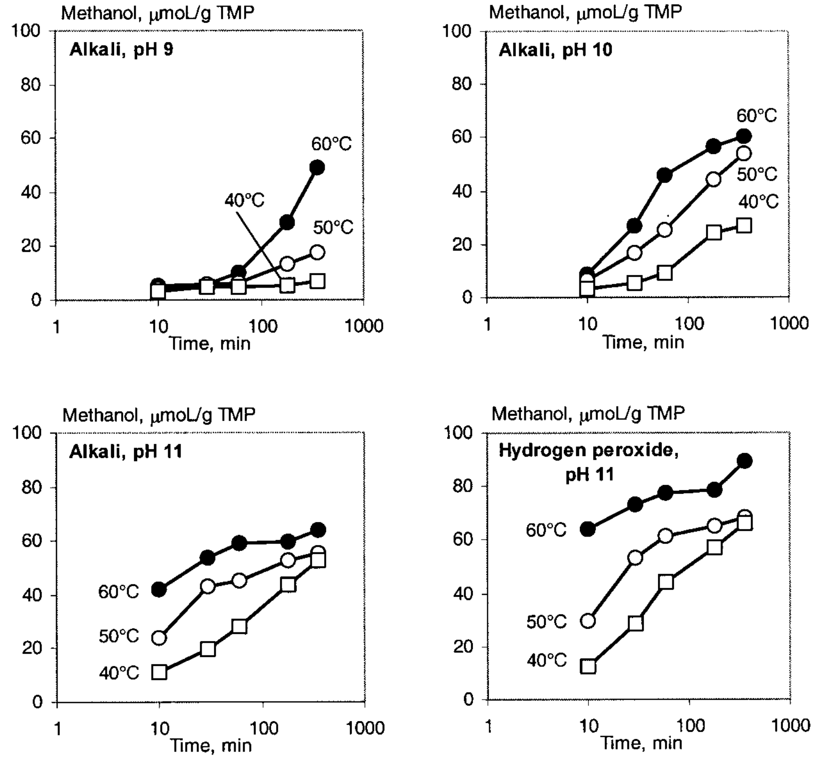

Figure 2. Release of methanol from TMP.

Extended treatment at 60°C released even more methanol and reached a level of 90 μmol/g TMP after 6 h. At 40–50°C, this effect of hydrogen peroxide was smaller, giving a maximum methanol release of 60 μmol/g TMP, that is similar to treatment with only alkali.

The higher rate of methanol removal at 60°C compared to 40–50°C is probably related to an increase in peroxide-induced oxidation of lignin. Methoxyl groups in lignin can be cleaved to some extent by hydrogen peroxide in alkaline media.[15]

Release of Hemicelluloses and Pectins

Information about the composition of alkali-soluble polysaccharides was obtained by acid methanolysis followed by GC analysis. Galacturonic acid and xylose were predominant units in the polysaccharides released from ‘‘clean’’ TMP fibres into water. Their proportions differed markedly from that of corresponding carbohydrates in TMP fibres (Fig. 3).

It is generally believed that in spruce wood galacturonic acids are mainly in the pectic acids. Pectic acids, i.e., polygalacturonic acids, are built up mainly of galacturonic acid units, but can also contain some rhamnose units.[16] In native spruce wood the polygalacturonic acids are methylesterified in varying degree.[14,17]

The amount of pectic acids (expressed as galacturonic acid units) in water increased substantially at pH higher than 9 (Fig. 4). However, even at pH 9 and 60°C, galacturonic acid was slowly released from TMP, starting after 1 h of treatment. Six hours of treatment at pH 9 and 60°C resulted in the release of 1.5 mg/g TMP galacturonic acid units into water. At pH 10–11 the rate of galacturonic acid release was notably higher and varied much with temperature. However, after a high initial rate during the first 60 min at pH 11 and 60°C, the release levelled off at 3.7 mg/g TMP. Addition of hydrogen peroxide affected both the rate and final yield. With hydrogen peroxide at 60°C the major part of polygalacturonic acid was released already after 30 min of treatment and after 1 h it levelled off at 4.8 mg/g TMP. At 40–50°C, however, hydrogen peroxide showed little effect on galacturonic acid release.

It is known that peroxide can decompose galacturonic acids, resulting in the formation of low-molar-mass acids and carbon dioxide.[18]

The major part of pectic acids still remained in the fibres even after extended alkali treatment, even with hydrogen peroxide. The nature of this restricted pectic acid removal is not yet known. However, it can be suggested that this phenomenon is a reflection of pectin topochemistry.

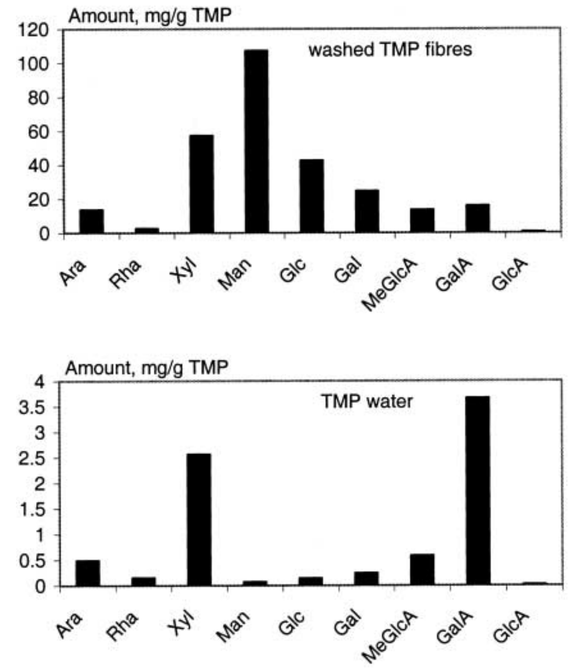

Figure 3. Composition of sugar units in hemicelluloses and pectins in TMP fibres, and in material released into water after 6 h treatment at pH 11 and 60°C, determined by acid methanolysis and GC.

Hoffman and Parameswarran[19] and then Westermark and Vennigerholz[17] clarified in detail the morphological distribution of acidic and methylesterified pectin in spruce and pine wood cells. Contrary to earlier suggestions,[20] they concluded that the methylesterified pectin is distributed evenly in the primary cell wall, while acidic forms occur occasionally at the middle lamella cell corners, in the tori of the bordered pits and in the ray cells. It has also been assumed some correlation between carboxylic groups in acidic pectin and metal ions.[14] Still, it is believed that cohesion of acidic pectin in naturally occurring wood is mostly due to cross-links (so-called "egg-box" structures) via divalent metal ions (calcium ions most frequently mentioned).[6,14] It is also known that reagents, which can form complexes with divalent ions (for instance, soluble salts of oxalic, citric and phosphoric acids as well as diethylenetriaminepentaacetic acid (DTPA) and other chelating agents) will result in partial pectin removal.[20] In our case, a small amount of DTPA was added before treatment with

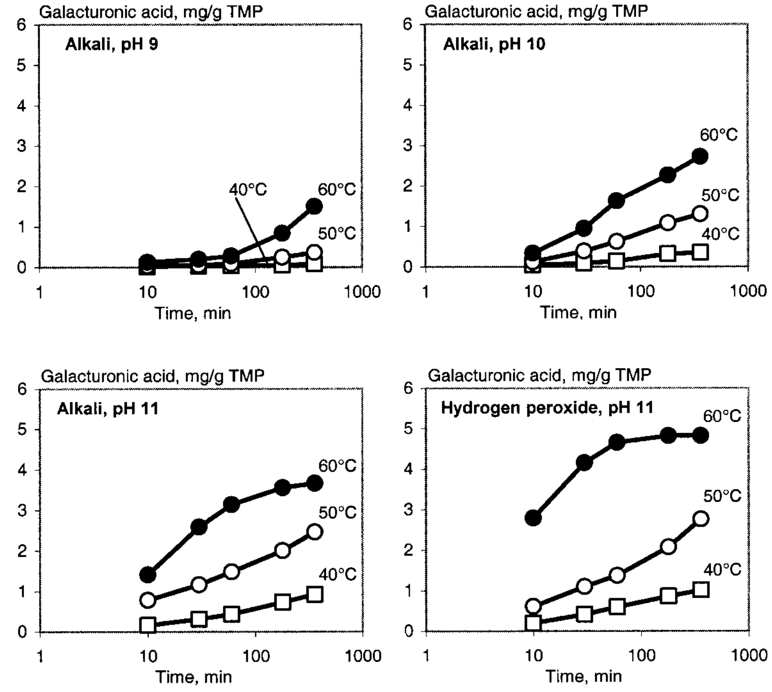

Figure 4. Release of pectic acids, determined as galacturonic acid, from TMP.

hydrogen peroxide. Oxalic acid is a typical product of extensive oxidation of aromatic part in wood, formed during treatment with hydrogen peroxide at alkaline conditions. However, galacturonic acid units were initially effectively released into water during treatment with alkali only, i.e., without the presence of oxalic acid and/or DTPA. Hence the main pathway of the dissolution of pectin, at least at alkaline conditions without hydrogen peroxide, is governed by a mechanism other than divalent ion removal.

Dissolution of pectins at alkaline conditions probably require their partial depolymerisation. The polygalacturonic acids released from TMP in alkaline conditions have a DP less than 100.[21] Polygalacturonic acids dissolved in alkaline peroxide bleaching have an even lower molar mass, with an average DP of about 20.[3] The polygalacturonic chain can be split by β-elimination, but the reaction requires the presence of methoxyl groups and is inhibited by their saponification.[22,23] Accordingly, when the methanol removal from pectin is complete, pectin dissolution should reach a plateau as the β-elimination reaction stops.

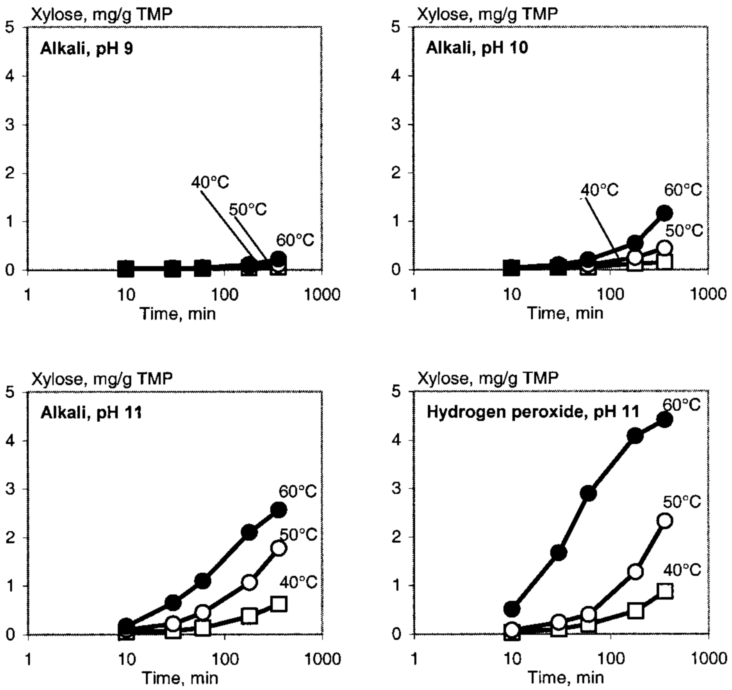

Figure 5. Release of xylan, as xylose units, from TMP.

Xylans were released into water at a markedly slower rate than pectic acids (Fig. 5). The release started at pH 10 and was more extensive at higher temperatures, which is in agreement with previous findings.[24]

The effect of hydrogen peroxide on the dissolution rate of xylans was notable at 40–50°C and drastic at 60°C, especially at the initial stages. After 1 h at pH 11 about three times more xylose units (2.9 mg/g TMP) were released into water than with alkali only.

After extended treatment (6 h) at pH 11 the effect of hydrogen peroxide on dissolution of xylans was also considerable; about 2.6 mg/g TMP and 4.4 mg/g TMP of xylans were released into TMP water, respectively, without and with peroxide (Fig. 5). However, that is only a small part (4–8%) of the total amount of xylans in TMP. It is substantially smaller than the corresponding value for pectin, which was about 25–40%. There may be several reasons for this difference. One reason may be that native xylans are chemically stable at the applied mild conditions and there is no polymer degradation. Another reason could be mass transfer limitations due to the DP and branched polymer structure.

In that case the dissolution of polymer can be governed by swelling of the fibre material. However, the dissolution of xylans may also be related to their association to the lignin in the cell wall. Even if the origin of the covalent linkages in so-called lignin–carbohydrate complexes is still a controversial issue, a frequently suggested linkage is the ester bond (Ref.[12], pp. 167–181). According to Obst,[7] mild alkali treatment cleaves 10–20% of the lignin-carbohydrate bonds, and these are proposed to be mainly uronic acid ester linkages to lignin. Cleavage of ester bonds between lignin and arabino-(4-*O*-methylglucurono)-xylan,[25,26] most probably increase the solubility of the polymer in mild alkali.

Release of Lignin

Lignin or lignin-like substances, here measured by UV-adsorption, are dissolved at alkaline conditions (Fig. 6). Although a small part of the lignins, 1.3 and 1.6 mg/g TMP, respectively, dissolved already in

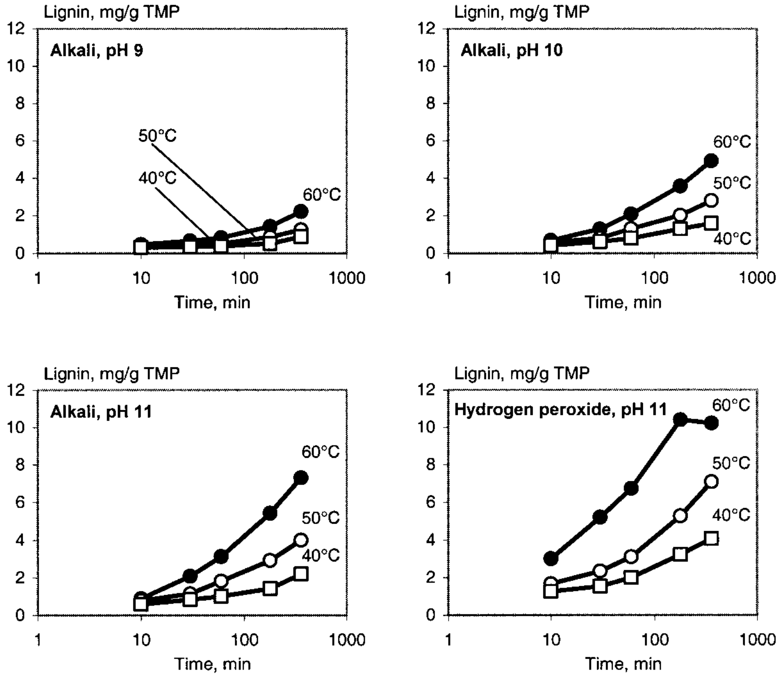

Figure 6. Release of lignin material from TMP.

hot water and was removed during TMP washing,[27] lignin material still mainly remained in the fibres. The amount of dissolved lignin after 1 h of treatment was small at pH 9, but notable at pH 10 and 11. Even if the dissolution rate was relatively low, the dissolution continued during extended treatment. After 6 h of treatment at pH 11 and 60°C this leaching accounted for substantial release of lignin in water. The rate of lignin release from TMP fibres was, probably, governed by diffusion limitations, in a similar way as reported by Favis and Goring[28] regarding the leaching of lignin macromolecules from the fibre walls of unbleached kraft pulp. However, some cleavage of the most alkali-sensitive bonds, such as esters in lignin–carbohydrate complex (LCC) or even ethers at C_α in the side chains of guaiacyl–propane units, may be expected. The latter can split off already in 0.05 M NaOH even at room temperature.[29,30]

A much higher rate of lignin dissolution was obtained with hydrogen peroxide. The yields after 1 h of treatment almost doubled with hydrogen peroxide compared to mere alkali. It was most considerable at 60°C (ca. 6.4 mg/g TMP) and levelled off at ca. 10.4 mg/g TMP.

The release of lignin during alkali treatment with or without hydrogen peroxide can be considered as a result of both wood swelling and chemical degradation reactions. In an earlier study was found that lignin dissolved in water during peroxide bleaching of TMP had a notably lower molar mass than spruce milled wood lignin (MWL), having an average 5–8 phenyl propane units with a rather narrow mass distribution.[27] Furthermore, the lignin dissolved during peroxide bleaching was structurally changed and notably oxidised. Such drastic changes in lignin structures do probably not take place in the absence of hydrogen peroxide.

Overall Loss of Fibre Material

The overall loss of fibre material from "clean" TMP during alkali treatment is given in Table 1. The dissolution of organic material was strongly dependent on both pH and temperature. The maximum loss of organic substances occurred after 6 h of treatment at pH 11 and 60°C (35.9 mg/g TMP).

At the initial stage of treatment at pH 11, methanol and acetic acid comprised most (about 80%) of the dissolved material. Later, when the alkali-induced hydrolysis of corresponding esters was completed, the dissolved material was enriched with carbohydrates and lignin. After 6 h of treatment at pH 11 and 60°C the portion of methanol and acetic acid in soluble fibre material decreased the number to 57%. Hydrogen peroxide affected the level and rate of fibre material dissolution, but changes in the

Table 1. Dissolution of fibre components from washed TMP, mg/g TMP.

		pH 9					pH 10					pH 11					Hydrogen peroxide, pH 11				
		Treatment time (min)					Treatment time (min)					Treatment time (min)					Treatment time (min)				
Temp. (°C)	Organic material	10	30	60	180	360	10	30	60	180	360	10	30	60	180	360	10	30	60	180	360
60	Methanol	0.2	0.2	0.3	0.9	1.6	0.3	0.9	1.5	1.8	1.9	1.3	1.7	1.9	1.9	2.0	2.1	2.3	2.5	2.5	2.9
	Acetic acid	0.6	0.8	1.0	2.2	5.0	0.7	3.5	7.7	14.6	16.7	9.0	16.5	18.3	18.3	18.7	14.6	16.9	17.3	17.4	17.6
	Carbohydrates	0.4	0.6	0.7	1.4	2.2	0.7	1.5	2.3	3.4	4.7	2.0	3.9	5.1	7.0	7.9	3.9	7.1	9.4	11.2	11.6
	Lignin	0.5	0.7	0.8	1.4	2.2	0.7	1.3	2.1	3.6	4.9	0.9	2.1	3.1	5.4	7.3	3.0	5.2	6.7	10.4	10.2
	Sum	**1.7**	**2.3**	**2.8**	**5.9**	**11.0**	**2.4**	**7.2**	**13.6**	**23.4**	**28.2**	**13.2**	**24.2**	**28.4**	**32.6**	**35.9**	**23.6**	**31.5**	**35.9**	**41.5**	**42.3**
	Analysed TOC[a]	0.8	1.1	1.3	2.7	5.0	1.1	3.2	6.1	10.4	12.8	5.5	10.2	12.3	14.6	16.6	10.3	14.1	16.3	19.6	20.0
	Measured TOC	0.6	0.8	1.3	2.8	5.2	1.3	3.2	6.0	9.6	12.4	4.9	9.5	11.2	14.4	15.4	12.2	16.8	19.2	23.4	23.8
50	Methanol	0.1	0.2	0.2	0.4	0.6	0.2	0.5	0.8	1.4	1.7	0.7	1.4	1.5	1.7	1.8	1.0	1.7	2.0	2.1	2.2
	Acetic acid	0.3	0.3	0.4	0.6	1.4	0.7	1.4	3.5	8.9	12.3	5.5	10.0	14.1	17.0	18.4	9.3	14.1	16.3	17.5	17.6
	Carbohydrates	0.4	0.3	0.4	0.6	0.8	0.5	0.8	1.2	1.8	2.3	1.2	1.8	2.4	3.8	5.3	1.0	1.8	2.2	4.2	6.3
	Lignin	0.4	0.5	0.5	0.9	1.3	0.6	0.8	1.3	2.0	2.8	0.8	1.2	1.8	2.9	4.0	1.7	2.4	3.1	5.3	7.1
	Sum	**1.2**	**1.3**	**1.5**	**2.5**	**4.1**	**2.0**	**3.5**	**6.8**	**14.1**	**19.1**	**8.2**	**14.4**	**19.8**	**25.4**	**29.5**	**13.0**	**20.0**	**23.6**	**29.1**	**33.2**
	Analysed TOC	0.5	0.7	0.8	1.3	2.0	1.0	1.7	3.1	6.2	8.4	3.6	6.0	8.5	11.0	13.0	5.7	8.6	10.4	13.2	15.3
	Measured TOC	0.5	0.5	0.7	1.4	2.0	0.9	1.9	3.0	5.8	7.8	3.7	6.3	8.5	10.3	12.3	6.5	9.9	11.6	15.8	18.5
40	Methanol	0.1	0.2	0.2	0.2	0.2	0.1	0.2	0.3	0.7	0.9	0.4	0.6	0.9	1.4	1.7	0.4	0.9	1.4	1.8	2.1
	Acetic acid	0.3	0.3	0.4	0.6	0.8	0.6	1.3	1.8	3.4	4.5	3.3	4.4	7.7	11.8	15.4	5.7	9.2	12.4	15.9	17.0
	Carbohydrates	0.3	0.3	0.3	0.3	0.4	0.3	0.4	0.5	0.8	0.8	0.4	0.6	0.8	1.5	2.1	0.4	0.8	1.1	1.8	2.5
	Lignin	0.3	0.4	0.4	0.5	0.9	0.4	0.6	0.8	1.3	1.6	0.6	0.8	1.0	1.4	2.2	1.3	1.5	2.0	3.2	4.1
	Sum	**1.0**	**1.2**	**1.3**	**1.6**	**2.3**	**1.4**	**2.5**	**3.4**	**6.2**	**7.8**	**4.7**	**6.4**	**10.4**	**16.1**	**21.4**	**7.8**	**12.4**	**16.9**	**22.7**	**25.7**
	Analysed TOC	0.5	0.6	0.6	0.8	1.2	0.7	1.2	1.5	2.9	3.6	2.1	2.8	4.4	6.8	9.1	3.5	5.4	7.3	10.0	11.4
	Measured TOC	0.4	0.4	0.6	0.6	0.9	0.6	0.8	1.2	2.8	3.0	1.8	2.7	3.9	7.0	8.5	4.3	6.8	8.8	11.9	13.3

[a] TOC in mg/g pulp, calculated from the sum of analysed components.

composition during treatment still remained essentially the same as with only alkali.

At pH 10, however, changes in the relative composition of the released material differed from the above. After 10 min of treatment at different temperature, soluble fibre material consist of only 40–50% of methanol and acetic acid. After extended treatment 6 h that number steadily increased up to about 70%. At pH 9, the changes in composition of dissolved fibre material during treatment was substantial at 60°C when the contribution of methanol and acetic acid there increased from 47% (10 min) to 60% (360 min).

The good agreement of measured and calculated TOC values supported the reliability of the analytical results. However, there was an appreciable difference between measured and calculated TOC values after treatment of TMP at alkaline conditions with hydrogen peroxide. For instance, if the calculated amount of dissolved fibre material at 60°C (6 h) levelled off at a TOC value 20.0 mg/g TMP (corresponding to 42.3 mg/g TMP), the measured TOC value levelled off at 23.8 mg/g TMP. Probably, the reason of this divergence is the formation of oxidised products induced by hydrogen peroxide. GC analysis verified that peroxide bleaching released miscellaneous low-molar-mass acids into water, especially hydroxyacetic, malic, ethanedioic, 3-hydroxypropanoic, and propanedioic type acids (Fig. 7). If assumed that the observed divergence is the consequence of formation of those acids, the estimated amount based on total oxy-acids TOC data should correspond to approx. 8 mg/g TMP (after 6 h at 60°C). In that event, such acids generated during treatment with hydrogen peroxide are important factors for the overall alkali consumption and material loss. The oxidation proceeded rapidly at the initial stage of treatment, about half the low-molar acids being released already after 10 min of treatment with hydrogen peroxide at 60°C.

Formation of Anionic Charge Groups in Water Phase and Fibres

The dissolution of anionic polymers was relatively slow, being notable only at pH 10 and 11 (Fig. 8). At 40°C the dissolution was almost negligible at pH 10, and just barely increased at pH 11. Accordingly, the most substantial release of anionic polymers occurred at 60°C and pH 11, when the cationic demand of dissolved substances approached a maximum level of 55 μeq/g TMP after 6 h.

Dissolved pectic acids (i.e., polygalacturonic acids) contributed to a major part of the measured cationic demand of the water phase.

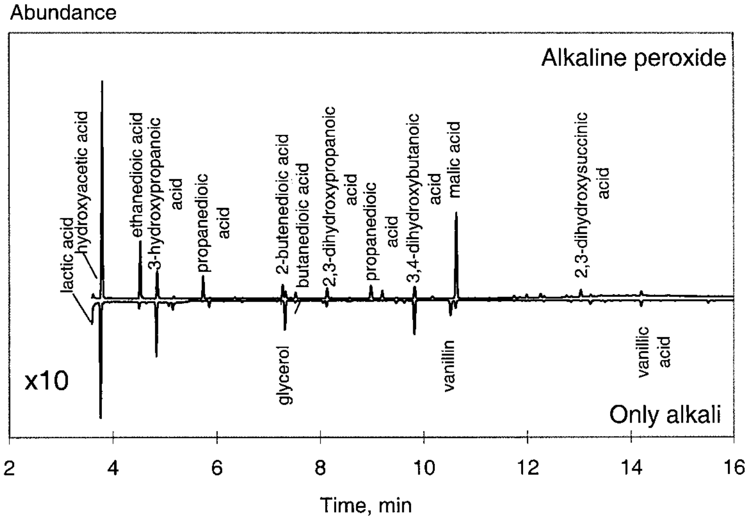

Figure 7. GC chromatograms of organic acids released into water during alkali treatment of TMP, with and without hydrogen peroxide, at starting pH value 12 and temperature 60°C.

After 1 h at pH 11 and 60°C, the estimated contribution of pectic acids covered 42% of the measured cationic demand. However, the contribution gradually decreased during extended treatment, being about 33% after 6 h.

Addition of hydrogen peroxide at pH 11 and 60°C resulted in a doubled amount of charged groups in dissolved polymers compared to treatment with mere alkali. It also dramatically accelerated their removal during the first 30 min, during which about 75% of the overall charged groups were released into the water phase. The contribution of dissolved pectic acid to the measured cationic demand was not as large as it was after treatment with only alkali. Hence it appears that during peroxide bleaching partly oxidised polymeric substances, probably lignin-derived, become dominant contributors to the so-called "anionic trash."

In untreated TMP fibres the naturally occurring anionic charge was determined to 83 μeq/g TMP. The theoretical contribution of both 4-*O*-methylglucuronic (12.8 mg/g TMP) and glucuronic (0.8 mg/g TMP) acids to that initial charge is calculated to 65 μeq/g TMP. If the amount of free carboxylic groups in pectins based on our estimation that the degree of methylesterification is about 75%, the theoretical contribution

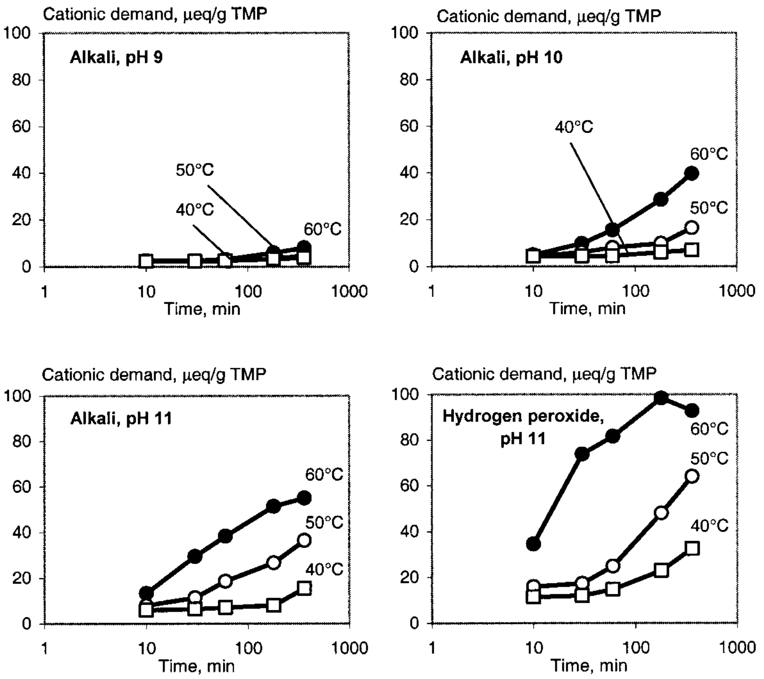

Figure 8. Cationic demand of acidic polymers released into water from TMP.

of naturally occurring pectins to the anionic charge was about 21 μeq/g TMP. It seems that the uronic acids are the main structures accounting for the charge in untreated TMP fibres.

The content of charged groups in fibres increased much faster than the amount of anionic polyelectrolytes in water (Fig. 9). The cationic demand in fibres started a steady rise already at pH 9 and had, after extended treatment at 60°C, increased from 84 μeq/g TMP to 139 μeq/g TMP. However, the formation of new carboxylic groups at pH above 10 was more extensive, since about the same fibre charge was attained after 50 min of treatment. At pH 11 and 60°C, new anionic groups were 135 μeq/g TMP after 10 min, and levelled off at 187 μeq/g TMP after 1 h. Charged groups were formed with the same kinetics as the release of methanol and acetic acid (cf. Figs. 1 and 2), supporting the suggestion that naturally occurring esters (methyl esters in pectin, esters of uronic acids in LCC, and probably, even lactonised form of those acids) constitute the main source for charged groups formed in mildly alkali-treated TMP.[31,32]

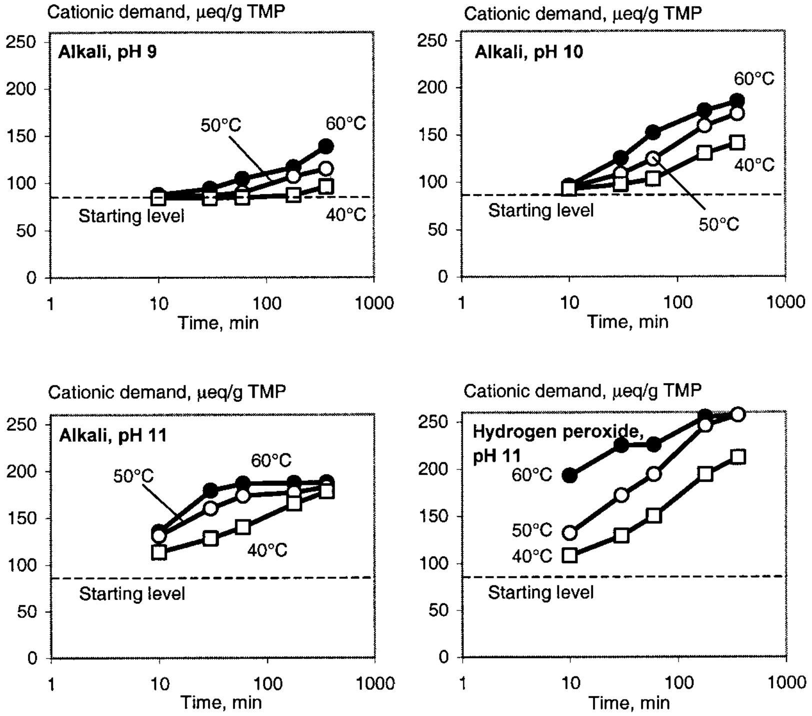

Figure 9. Formation of acidic groups in TMP fibres.

Because of the alkali-induced dissolution of pectins, the content of residual galacturonic acid units in fibres decreased from 16 mg/g TMP to 11.2 mg/g TMP after 1 h at pH 11 and 60°C (Fig. 10). Since the alkaline hydrolysis of methyl esters in pectins is complete after 1 h (Fig. 2), that amount of demethylated residual galacturonic acid units theoretically corresponds to a cationic demand of about 57 μeq/g TMP, and accordingly, to about a half of the measured charge increase in fibres.

In the presence of hydrogen peroxide, the changes in fibre charge were dramatically faster and more extensive. After 10 min the charge had increased up to 193 μeq/g, i.e., more than the maximum charge obtained with alkali only (Fig. 9). Thirty minutes of treatment was enough to reach a plateau at 225 μeq/g TMP. Nevertheless, due to continuous peroxide-induced oxidative processes on fibres, the extended (3 h and longer) treatment resulted in additional increase of TMP fibre charge, which steadily increased up to 255 μeq/g TMP.

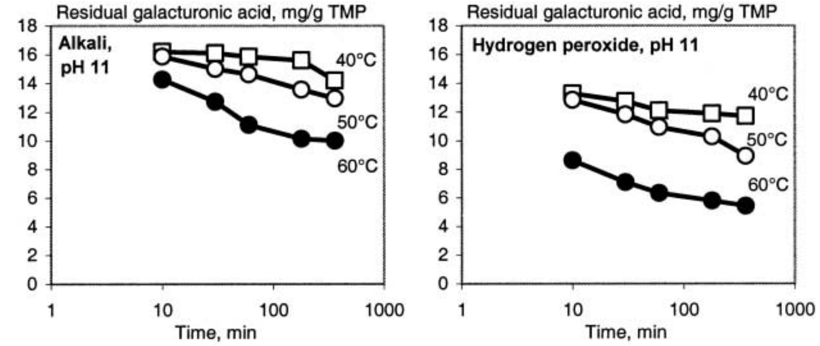

Figure 10. Content of residual galacturonic acid units in washed TMP fibres.

CONCLUSIONS

Alkaline Treatment

- The major organics released into water during alkali-treatment of "clean" TMP fibres are acetic acid, carbohydrates (mainly pectic acids and xylan), and low-molar-mass lignin. After 3 h of treatment at pH 11 and 60°C, the release of these components results in overall loss of fibre material up to 30 mg/g TMP.
- The most rapid chemical transformations in the fibres during mild alkali are cleavage of ester bonds leading to the release of acetic acid and methanol. Kinetic curves demonstrated complete hydrolysis after 1 h of treatment at pH 11 and 60°C. After 10 min of alkali treatment about 50% of acetic acid and methanol were released.
- The profiles of charge increase in fibres during alkali treatment demonstrate kinetics similar to the release of methanol. This verifies the importance of alkaline hydrolysis of methyl esters in pectin for the substantial formation of carboxylic groups, i.e., increased charge on fibres.
- Carbohydrates released into water are mainly pectic acids and xylans. However, the amounts released were only a small portion of their total amounts in TMP fibres. Nevertheless, pectic acids are the main source for cationic demand in waters from alkali-treated TMP.
- The mechanism of the dissolution of pectic acids is not yet clear. It seems to be related to alkali-induced β-elimination cleavage on

the polygalacturonic chain. Saponification is, probably, a competitive and inhibiting factor for the dissolution of pectic acids.
- It can be suggested that lignin removal from TMP is governed by physico–chemical mechanisms, such as swelling and diffusion.

Peroxide Bleaching

- Most of the dissolution of fibre material occurs already during the first 30 min. Hydrogen peroxide, compared to alkali only, is responsible for about one third of the total dissolution. After 3 h of bleaching, up to 40 mg/g TMP of fibre material was released into water.
- Clearly more lignin is released upon peroxide addition. The dissolution continues further between 30 and 360 min. This indicates that peroxide degrades lignin at pH 11, which then slowly diffuses out from the fibres.
- The formation of new carboxyl groups in the fibres followed similar kinetics as deacetylation and demethylation. Peroxide increased the formation of carboxyl groups.
- Although oxidative processes on fibres during treatment with peroxide are extensive and result in acceleration of chemical alteration of TMP, all main changes on fibres during peroxide bleaching occur due to the alkaline conditions.

EXPERIMENTAL

Materials

Thermomechanical pulp from Norway spruce (*Picea abies* L.) was sampled in a Finnish mill, after the second-stage refiner at ca. 35% consistency. The sampling was done during winter (January 1998), and the pulp was stored in a freezer at −24°C until needed.

Fibres for solid-phase microextraction (SPME), coated with 75 μm Carboxen-PDMS, were obtained from Supelco Inc., Bellefonte, PA, USA.

Ion-exchange resin, DOWEX 50W × 8 (p.a., 50–100 mesh, H^+-form), was obtained from Fluka Chemie AG., Buchs, Switzerland.

1,5-Dimethyl-1,5-diazaundecamethylene polymethobromide (polybrene) was obtained from Sigma Chemicals Co., St. Louis, MO, USA.

Potassium polyvinyl sulfate (KPVS) was obtained from Wako Pure Chemical Industries Ltd., Osaka, Japan.

Methyl-*tert*-butyl ether was of HPLC grade. Other chemicals were of pro analysis grade.

Methods

Washing

The TMP was freeze-dried and extracted in a Soxhlet apparatus with hexane–acetone (9:1 v/v) for 24 h to remove lipophilic material. In order to remove water-soluble substances (hemicelluloses and low-molar-mass aromatics) and obtain ‘‘clean’’ fibres, the TMP was thoroughly washed with distilled water five times. The pre-extracted TMP was suspended in distilled water (pH 5.5) at 60°C at 2% consistency and agitated 3 h with a blade propeller (ca. 200 rpm). The TMP suspension was filtered under vacuum on a Büchner funnel with a paper machine wire. To prevent the loss of fines, the filtrate was passed twice through the formed fibre mat. The TMP was re-suspended in distilled water and the washing procedure was repeated. The overall Total Organic Carbon (TOC) value of the substances released into water during washing was 157 mg/g TMP. The TOC value of the final filtrate was 4 mg/L. As a last step, the TMP fibre mat was disintegrated into small pieces (ca. 20–30 mm), air-dried, and stored in the dark at +4°C.

Treatments

Treatment of TMP fibres at alkaline conditions, with and without hydrogen peroxide, was performed in a 250-mL reaction vessel, equipped with a screw cap and an elastic silicon rubber septum. A Pt-100 temperature sensor, a pH electrode and a PTFE capillary tube for the inlet of chemicals were hermetically adapted through the septum. The reaction vessel was placed on a magnetic stirrer/hot plate.

Prior to treatment, the TMP fibres (4 g o.d. TMP in 192 mL of distilled water) were re-suspended at room temperature and kept overnight. The suspension was stirred at 150 rpm and heated until constant temperature (40, 50, or 60°C) was reached. The constant pH (9, 10, and 11) value was adjusted in less than 1 min by the addition of 0.5 M NaOH through the inlet capillary tube. When peroxide was used, 0.4 mL at 0.025 g/mL DTPA, 0.2 mL at 0.01 g/mL $MgSO_4$, 1.2 mL at 0.1 g/mL sodium silicate, and 4 mL at 0.03 g/mL H_2O_2 were mixed in a bottle, the mixture was injected by a glass syringe, and the pH value was adjusted as above. The reaction was stopped by acidification with 6% SO_2–water to pH 5.5–5.8. The suspension was cooled on an ice-water bath, and an aliquot of internal standard (2 mL 0.005% 2-propanol in water) was added. The TMP suspension was periodically shaken during 60 min, and stored prior to analysis for 24–48 h in the dark at +4°C.

Sample Preparation

To quantify methanol, care was taken during the TMP-water filtration step. About 20 mL of treated, neutralized, and cooled TMP suspension with added internal standard was filtered under pressure using a glass syringe through a 0.2 μm nylon/glass syringe filter, and exactly 2.5 g of filtrate was immediately transferred to a vial for GC analysis.

Furthermore, the main part of the suspension was filtered three times under low vacuum on a Büchner funnel with a wire. Particle-free filtrates were obtained and stored in the dark at +4°C.

The filtered fibres formed a mat, which was additionally washed with about 2 L of distilled water (the conductivity of water from 1% suspension of washed pulp was below 15 μS/cm). The TMP fibres were then freeze-dried and kept in the dark at +4°C.

Analyses

Total Organic Carbon (TOC) was measured with a TOC-5050 Analyzer (Shimadzu Corp., Japan).

The sugar composition of hemicelluloses and pectins was determined using methanolysis (2 M HCl in dry methanol), followed by gas chromatographic (GC) analysis of TMS-derivatives of corresponding sugar monomers formed.[33] The samples were freeze-dried prior to methanolysis.

Low-molar-mass lignin content in TMP-waters was determined by UV-absorption (Lambda 3 UV/VIS Spectrophotometer, Perkin-Elmer Co., USA) at 280 nm. Well-characterised preparations of lignin, isolated previously from unbleached and bleached TMP-waters[27] were used for calibration.

Acetic acid was determined by GC. In order to transform the salts (acetates) to free acids, TMP-water (4 mL or 8 mL) with 1 mL of 0.5 mg/mL of *iso*-butyric acid (internal standard) was passed through a column (10 mm i.d.) packed with cation exchange resin, DOWEX 50W × 8. The free acids were eluted with distilled water and titrated to pH 8 with 0.08 M tetra-*n*-butylammonium hydroxide (TBAH) and evaporated to dryness under vacuum, using three time addition of acetone. The TBA salts were converted into their benzyl esters by adding 1 mL solution of benzyl bromide in acetone (1:20).[34] The benzyl esters were analyzed by GC using an HP-5 (crosslinked 5% phenyl methyl siloxane) fused-silica capillary column (25 m × 0.2 mm ID, film thickness 0.11 μm) and FID. Hydrogen was used as a carrier gas. The oven temperature profile was: initial temperature 80°C (hold 1 min), final temperature 285°C, temperature increase rate 8°C/min. The injector temperature was 260°C, and the detector temperature 290°C. The samples were injected using an autosampler (Varian 8200).

Methanol was quantified using headspace solid-phase microextraction (SPME), followed by GC analysis on a polar phase (INNOWAX) capillary column.[35]

Cationic demand (CD) of TMP fibres was determined by polyelectrolyte titration. Zero point five gram o.d. TMP was soaked overnight in 29.5 g of distilled water and further stirred for 3 h. Twenty grams of 0.01 N polybrene solution was slowly added to the suspension and the stirring was continued for 2 h. The suspension was centrifuged (30 min, 1500 rpm) and an aliquot (2–4 mL, exact volume measured) of the supernatant was titrated using 0.0005 N potassium polyvinyl sulphate (KPVS) as anionic polymer with a Mütek particle charge detector 03. TMP-water samples, containing dissolved and colloidal substances were mixed with 0.0005 N polybrene directly in the measuring cell and were then titrated with KPVS.

Conductivity of TMP waters was measured using a Microprocessor conductivity meter RE 387 Tx, Series 3 (EDT Instruments Ltd., Dover, UK).

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