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Selective froth flotation of pitch components from spruce TMP process water

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SUMMARY

Selective removal of dissolved and colloidal pitch components from an unbleached thermomechanical pulp (TMP) pressate by addition of a cationic foaming agent, dodecyltrimethylammonium chloride (DoTAC), and subsequent froth flotation was assessed. The experiments were conducted with varying pH, temperature, and concentrations of DoTAC and calcium. The concentrations of pitch components, lignans, and dissolved polysaccharides were determined before and after flotation.

All pitch components were removed more efficiently by flotation at pH 5 and 3.5 than by flotation at pH 7.6. Resin and fatty acids were removed to a higher degree than neutral pitch substances at all the tested pH levels. Most of the water-soluble uronic acids and galactoglucomannans stayed in the TMP water after flotation.

Froth flotation with DoTAC was an effective way of selectively removing colloidal and dissolved pitch. Removal of pitch, especially of resin acids, at an early stage should be beneficial to the overall papermaking process.

KEYWORDS:
Colloidal pitch, wood resin, mechanical pulp, flotation, anionic trash

INTRODUCTION

During production of mechanical pulps, such as thermomechanical pulp (TMP), a wide variety of wood components are either dissolved or suspended as water-insoluble particles, in the process water *(1-4)*. These wood components are mainly hemicelluloses and extractives of hydrophilic or lipophilic nature and can be described as 'dissolved and colloidal substances' (DCS).

Mixtures of lipophilic extractives are commonly known as pitch. About 80% of the pitch enters the paper machine as droplets of colloidal dimensions, and is referred to as colloidal pitch. Uncontrolled aggregation of colloidal pitch is detrimental in papermaking and is commonly linked to process disturbances such as formation of deposits and overall runnability problems *(4, 5)*. The colloidal pitch droplets consist of two distinct parts; a core consisting of the most hydrophobic components, i.e. triglycerides and steryl esters, and a surface layer of surface active components, i.e. resin and fatty acids (RFAs) *(6, 7)*.

The colloidal pitch droplets are electrostatically stabilised by the anionic charges of dissociated carboxyl groups in the RFAs; the dissociation is in turn a function of pH. The electrostatic stability of colloidal pitch is sensitive to electrolytes. Higher valence metal ions impede the colloidal stability of the pitch more than lower valence metal ions *(8)*. The presence of TMP fibres further lowers the colloidal stability of pitch related to calcium-induced aggregation *(9)*.

A very important factor in the behaviour of pitch is pH, since the solubility of RFAs is linked to the bulk pH *(10, 11)*. Studies have shown that the phase distribution of RFAs between colloidal pitch droplets and the water phase is a function of pH, electrolyte concentration, and pitch composition *(12, 13)*. Calcium was found to shift the phase distribution of most RFAs towards much higher pH, and it was also shown that calcium soaps of resin acids were more soluble in water than calcium soaps of fatty acids *(14)*.

Electrophoretic measurements of pitch emulsions have shown that the anionic charge density of the colloidal droplets increased with increasing pH, while the size of the colloids remained unaffected by pH *(15)*. Hence, the electrostatic stability of the colloidal pitch droplets related to calcium-induced aggregation was higher at higher pH levels *(9)*.

Water-soluble hemicelluloses released from Norway spruce (*Picea abies*) during mechanical pulping, especially galactoglucomannans (GGM), have been shown to sterically stabilise colloidal pitch droplets *(8, 9, 16-19)*. Deacetylation of GGM at alkaline conditions, as in peroxide bleaching, severely impairs the solubility of GGM in water, rendering it unable to stabilise colloidal pitch. A high concentration of water-soluble GGM is generally considered beneficial for the runnability of the paper machine.

Anionic carbohydrates, containing uronic acids, are also released from TMP during mechanical pulping. Galacturonic acid is, for instance, found in wood pectins. The reported amount of pectins in Norway spruce is only about 1 to 2%, but these are still of importance in papermaking, since uronic acids are the main contributors to the anionic charge of mechanical pulps *(20-23)*.

Dissolved anionic carbohydrates, as well as colloidal pitch, are generally considered to be 'anionic trash' in papermaking since they consume expensive retention chemicals (24). Removal of colloidal pitch and dissolved anionic carbohydrates could therefore benefit the papermaking process. Several alternatives have been proposed, such as binding of pitch and anionic carbohydrates to the fibre material by polymers or coagulants, sorbing them onto talc, passivation of the colloidal pitch by treatment with protein based detackifier, or removing these substances from the process waters by ultrafiltration or flotation (19, 25-29).

Flocculation and subsequent flotation of pitch has been investigated with a wide variety of polymers and coagulants in combination with dissolved air flotation (DAF) for different pulp and paper processes (19, 30-34). DAF with added bentonite, polyaluminium chloride (PAC), or polyethylene oxide and phenol formaldehyde resin (PEO/PFR) was capable of removing pitch from newsprint mill process waters derived from *Pinus radiata (30)*. About 70 to 80% of the total pitch could be removed, and this experimental setup worked well for fibre-bound and colloidal pitch. Removal of colloidal pitch from peroxide-bleached TMP water from Norway spruce by PAC, polyacrylamide (PAM) /bentonite or PEO/PFR and subsequent DAF treatment showed that the pitch could be effectively removed from the process water (32). DAF experiments with added cationic polyacrylamide (C-PAM) and polydiallyldimethylammonium chloride (poly-DADMAC) successfully removed about 70% of the total pitch from pressate samples from Norway spruce chips (34). However, about 60% of the hemicelluloses were also removed by the DAF treatment. DAF in combination with polymers is thus not a specially selective process to remove pitch, since hemicelluloses and a lot of fines, which could be reintroduced to the process, will also be lost due to the flotation. It was, however, shown that substantial amounts of pitch could be removed by DAF treatment from *P. radiata* newsprint process waters even without addition of chemicals (30). Previously published results show that dissolved pitch components, i.e. mainly resin acids, are difficult to remove from the waters by flocculation and subsequent DAF (19, 30, 32). It was further shown that pH has a strong influence on the efficiency of removal of RFAs with DAF. The chemical composition, the mechanisms of the flotation, and the dose of the used additives dictates the optimal flotation conditions (25, 30, 32).

Froth flotation, or induced air flotation (IAF), was recently suggested for removal of pitch and manganese from TMP waters (35, 36) or directly from diluted mechanical pulps with added calcium (37). Froth flotation is commonly used in deinking flotation and an advantage of this flotation setup could possibly be lower material losses than in DAF (38). The aim of this study was to selectively remove dissolved and colloidal pitch and anionic carbohydrates from TMP process water after pulping, but before bleaching. The intention was further to leave the water-soluble GGM in the process water. The selective flotation would be accomplished by addition of a cationic foaming agent and subsequent froth flotation of TMP press water taken before the bleaching process, before any chemical changes take place in the DCS during the alkaline bleaching conditions. The concentration of dissolved and colloidal pitch, lignans, anionic carbohydrates, and water-soluble GGM was determined before and after flotation.

MATERIALS AND METHODS

The process water used in the experiments was received from a pulp mill in Sweden, producing thermomechanical pulp and wood-containing paper from Norway spruce (*Picea abies*). The process water, or TMP water, was taken from the press section before the bleaching tower. The TMP water was stored in 25-L canisters in a cold room (6 °C), for a maximum of 4 days, until used. The TMP water contained about 0.1% of fines, determined gravimetrically after filtration through a 200-mesh plastic wire.

The foaming agent used was dodecyltrimethylammonium chloride (DoTAC), which is a cationic surfactant. The DoTAC was received from China Innovation Group Co., Ltd, with a purity of > 99%. A stock solution of DoTAC was prepared by dissolving it directly in distilled water to a concentration of 10 g/L.

The flotation cell used in these experiments was a 20 L laboratory Voith cell. The principle of the flotation cell was froth flotation, which is commonly used for deinking of pulp. The cell consisted of a mixer at the bottom of a tank (Fig 1). Foaming was induced through 1340 rpm agitation and the formed aggregates were carried to the surface by induced air bubbles, or due to their density being lower than the density of water. The air flow into the flotation cell could be adjusted between 0 and 10 L/min.
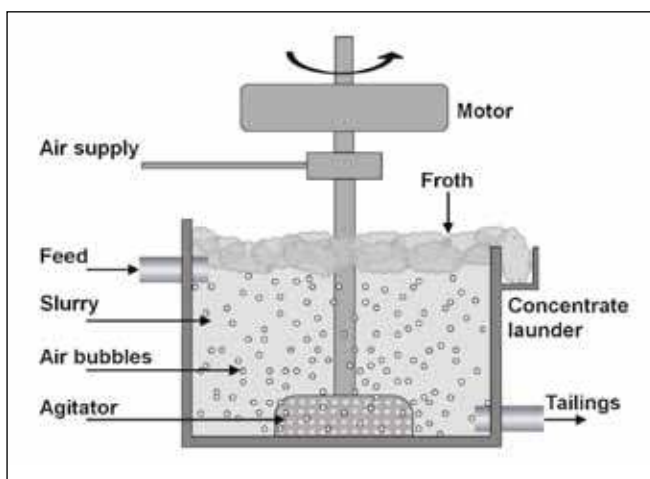

Fig 1. Schematic illustration of the laboratory froth flotation cell.

FLOTATION EXPERIMENTS

The TMP water was vigorously mixed and 6 L was poured into a beaker, stirred by a magnetic stirrer, and heated to either 20 or 50 °C. The pH was adjusted to 3.5, 5.1, or 7.6 with H_2SO_4 or NaOH. Different volumes of DoTAC stock solution was added to the beaker, and allowed to react for about 20 min under continuous mixing. The final DoTAC concentrations tested were 40, 60 or 80 ppm (mg/L). The mixture was poured into the flotation cell and the stirring was started. The flotations were performed for 60 min to ensure that the foaming was complete in the experiments. The formed foam was carefully pipetted out using a suction flask during the flotation. The air flow into the flotation unit was 0 L/min, except in the experiments assessing the influence of additional air flow where the air flow was 9 L/min. Samples of the TMP water were collected through the tailings tube after 60 min of flotation (Fig 1). The collapsed foam volume was measured in a graduated cylinder. Turbidity was measured directly after the flotation. Samples of the TMP

water were frozen for later determination of extractive and carbohydrate content.

ANALYSIS OF PITCH COMPOSITION

The samples were pipetted through a coarse metallic 20-mesh wire to remove most of the fines in the samples. An internal standard mixture containing equal amounts of heneicosanoic acid, betulinol, cholesteryl heptadecanoate, and 1,3-dipalmitoyl-2-oleyl glycerol in (tert-butyl)methylether (MTBE) was added to the samples *(39)*. H_2SO_4 was added to acidify the water samples, and the pitch components were extracted from the water samples with MTBE. The extractives in MTBE were then dried under N_2 gas, and silylated with pyridine, N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA), and trimethylchlorosilane (TMCS) for 45 min at 70 °C. The silylated extractives were analysed by gas chromatography (GC) on a short column (HP-1, 7 m by 0.53 mm) with on-column injection and detection by a flame ionization detector (FID). Individual resin and fatty acids were analysed on a long column (HP-1, 25 m by 0.20 mm) with split injection and detection by a FID detector.

ANALYSIS OF CARBOHYDRATES

The content of carbohydrates in the water samples was determined by GC after acid methanolysis *(40, 41)*. The samples were filtered through 0.22-µm nylon filters (MS NY Syringe filter, Membrane Solutions) to completely remove fines. The filtered samples were frozen and freeze-dried. Water-free 2 M HCl in methanol was added to the dry samples. The samples were placed in an oven at 100 °C for 3 hours and then neutralised with pyridine. Sorbitol in methanol was added as internal standard. The samples were silylated using pyridine, hexamethyldisilazane (HMDS) and TMCS at room temperature. The analysis of sugar units was conducted by long column GC (HP-1, 25 m by 0.20 mm) with split injection and detection by a FID detector.

ANALYSIS OF METAL IONS

The content of metal ions in the TMP water was analysed by inductively coupled plasma - optical emission spectrometry (ICP-OES). The determinations were conducted according to the SCAN standard method CM 38:96 on a Varian ICP-OES 720 instrument.

TURBIDITY MEASUREMENT

The turbidity of the TMP water samples was measured with a HACH RATIO/XR 43900 turbidimeter before and after flotation. The samples were allowed to sediment for 30 min before the measurements.

RESULTS

GC analysis of the TMP water before flotation revealed that the total concentrations of pitch and carbohydrates varied considerably between the received batches. The total concentration of dissolved and colloidal pitch in the TMP water varied between 100 and 270 mg/L, and the total concentration of carbohydrates between 1500 and 2000 mg/L. The TMP water also contained 185 to 200 mg/L of lignans. However, the composition of the pitch and the carbohydrates were quite similar in all of the different batches. The turbidity of the different batches of TMP water before flotation was between 1700 and 2500 NTU. Because of the variations in the received batches of TMP water,

the results are presented as relative concentrations; i.e. the residual concentrations of pitch components, carbohydrates and turbidity after the flotations, were compared with the original concentration in the batch of TMP water used in the flotation. About 70% of the pitch was composed of neutral substances, i.e. triglycerides, diglycerides and steryl esters (Fig 2). The fatty and resin acids constituted only about 9% and 18% of the total pitch, respectively. The dominating carbohydrates in the TMP water consisted of mannose, galactose, and glucose units. These three sugars constituted about 86% of the total carbohydrate content (Fig 2). The uronic acids galacturonic acid, glucuronic acid, and 4-O-methyl-glucuronic acid, made up only about 6% of the total carbohydrates. The main metals detected in the TMP water by ICP were 18 ppm of calcium (about 0.45 mM), 13 ppm of manganese (0.24 mM) and 3 ppm of magnesium (0.12 mM).
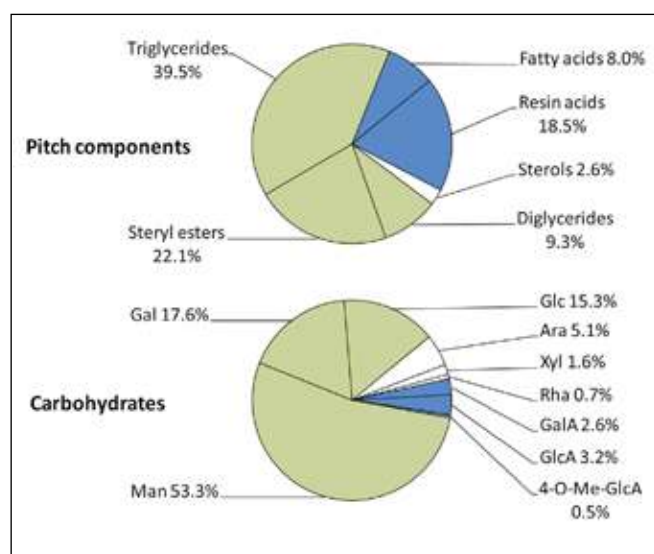

Fig 2. The composition of pitch components, and carbohydrates in TMP water before flotation. Man = mannose, Gal = galactose, Glc = glucose, Ara = arabinose, Xyl = xylose, Rha = rhamnose, GalA = galacturonic acid, GlcA = glucuronic acid, 4-O-Me-GlcA = 4-O-methyl-glucuronic acid.

FLOTATION AT DIFFERENT pH LEVELS AT 20 °C

Flotation experiments were performed at pH 3.5, 5.1, and 7.6 for 60 min to assess the influence of pH on the flotation setup. The temperature was 20 °C and the DoTAC concentration 80 ppm. The volume of the foam in the flotation at pH 5.1 was about 2% of the total TMP water volume (Table 1). At pH 3.5 and 7.6, the foam volumes were significantly larger than at pH 5.1. The maximum foam volume, i.e. 14% of the total volume of TMP water, was formed in the flotation at pH 7.6.

At pH 3.5, the residual turbidity was 10%, while the turbidity at pH 5.1 was 25%; and 50% at pH 7.6 of the original (Table 1). The concentration of total pitch, determined by GC, showed that about 14% of the pitch remained in the water after flotation at pH 3.5, and 37% at pH 5.1 (Table 1). Flotation at pH 7.6 had no significant effect on the total concentration of pitch, removing only about 2%.

About 20% of the neutral substances, i.e. triglycerides, diglycerides and steryl esters, remained after the flotation at pH 3.5, while the corresponding value at pH 5.1 was 50% (Fig 3). The residual concentration of neutral substances was 125% after flotation at pH 7.6, indicating that more neutral

pitch was dissolved from the fines at this pH. About 1% of the resin acids and 5% of the fatty acids remained in the water after flotation at pH 3.5, while the corresponding values at pH 7.6 were 20% for the resin acids and 40% for the fatty acids. The residual concentration of lignans was largely unaffected by the variations in pH (Fig 3).

About 84% of the uronic acids remained in the water after flotation at pH 3.5 (Table 1). Higher pH levels resulted in higher residual concentration of uronic acids. The concentration of water-soluble GGM increased during the flotation at all pH levels; the concentration of GGM in the TMP water was between 108 and 115% after the flotations (Table 1).

	Foam volume	Residual turbidity	Residual pitch	Residual uronic acids	Residual GGM
Flotation	%	%	%	%	%
pH 3.5	5	10	14 ± 1	84 ± 5	115 ± 5
pH 5.1	2	25	37 ± 1	101 ± 2	110 ± 3
pH 7.6	14	50	98 ± 2	112 ± 4	108 ± 3

Table 1. Foam volume and residual turbidity, pitch, and carbohydrates after flotation of TMP water - % of original. (The experiments were conducted with 80 ppm DoTAC at 20 °C. Foam volume = the collapsed volume of removed foam relative to the total volume of TMP water. Uronic acids = residual galacturonic acid, glucuronic acid, and 4-O-methyl glucuronic acid after flotation. GGM = residual galactose, glucose and mannose after flotation. The deviations of the determinations are shown as ± in the table.)
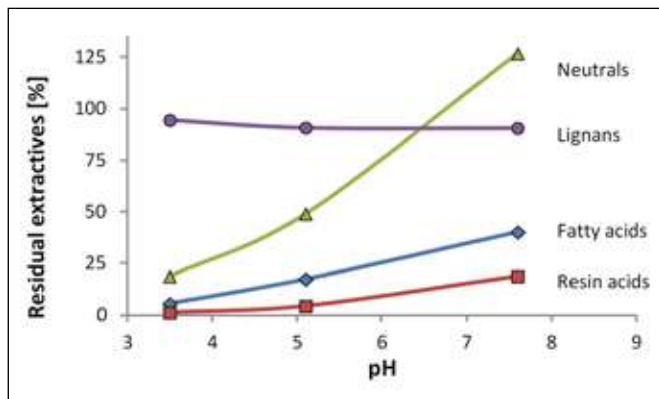
With 40 ppm DoTAC about 70% of the neutral pitch substances, 50% of the fatty acids and 35% of the resin acids remained in the water after flotation at pH 5.1 (Fig 4). Increasing the concentration of DoTAC to 80 ppm resulted in lower residual concentrations of RFAs from the TMP water; about 5% of the resin acids and 15% of the fatty acids remained in the water after flotation. Less neutral pitch was removed compared to the RFAs; about 50% of the neutral pitch remained in the TMP water after the flotation even with 80 ppm DoTAC (Fig 4).

	Foam volume	Residual turbidity	Residual pitch	Residual uronic acids	Residual GGM
Flotation	%	%	%	%	%
pH 5.1, 40 ppm	1	53	64 ± 2	81 ± 3	86 ± 1
pH 5.1, 60 ppm	2	38	53 ± 1	87 ± 1	93 ± 1
pH 5.1, 80 ppm	2	25	37 ± 1	101 ± 2	110 ± 3
pH 3.5, 40 ppm	2	35	27 ± 1	87 ± 0	96 ± 1
pH 3.5, 60 ppm	2	21	28 ± 0	85 ± 0	95 ± 1
pH 3.5, 80 ppm	5	10	14 ± 1	84 ± 5	115 ± 5

Table 2. Foam volume and residual turbidity, pitch and carbohydrates after flotation of TMP water. The experiments were conducted at pH 5.1 and 3.5 with 40, 60, and 80 ppm DoTAC at 20 °C. The deviations of the determinations are shown as ± in the table; ± 0 indicates deviation below 0.5%.
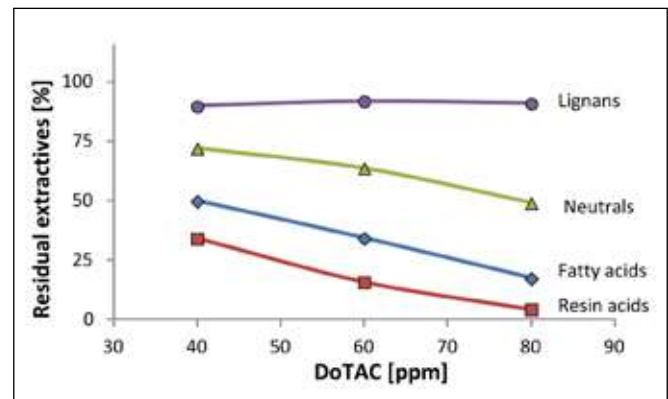

Fig 3. Residual extractives after flotation of TMP water, with 80 ppm DoTAC at 20 °C.

Fig 4. Residual extractives after flotation with varying DoTAC concentration at 20 °C and pH 5.1.

FLOTATION WITH DIFFERENT CONCENTRATIONS OF DoTAC AT 20 °C

The influence of the concentration of DoTAC on the flotation setup was assessed at pH 5.1 and 3.5. Flotation experiments were performed with 40, 60, and 80 ppm DoTAC at 20 °C for 60 min. At pH 5.1, the foam volumes were 1 to 2% at all DoTAC concentrations (Table 2). The lowest concentration of DoTAC, 40 ppm, lowered the residual turbidity of the TMP water to 53% at pH 5.1. Increasing the concentration of DoTAC from 40 to 60 or 80 ppm resulted in further decrease in residual turbidity, indicating that more colloidal particles were removed. Determinations of the total pitch concentration showed that 37 to 64% of the colloidal pitch remained in the water after flotation at pH 5.1 depending on the concentration of DoTAC (Table 2).

The influence of DoTAC concentration on the flotation setup was also assessed at pH 3.5, in the same way as the experiments at pH 5.1. At pH 3.5, the foam volumes with 40 and 60 ppm DoTAC were 2%, which was similar as in the flotations at pH 5.1 (Table 2). However, 80 ppm DoTAC resulted in a noticeable increase in foam volume, from 2% at 60 ppm to 5% at 80 ppm DoTAC.

At pH 3.5, the residual turbidity of the TMP water was 35% after flotation with 40 ppm DoTAC, i.e. significantly lower than at pH 5.1 (Table 2). Increasing the concentration of DoTAC resulted in a further decrease in residual turbidity, and the residual turbidity was only 10% after flotation with 80 ppm. GC analysis revealed that about 30% of the total pitch remained in the water after flotation with 40 and 60 ppm DoTAC, while

only 14% remained after flotation with 80 ppm (Table 2).
The residual concentration of uronic acids in the TMP water after flotation was found to be between 81 and 101%, increasing with increasing DoTAC concentration at pH 5.1, and about 85% at pH 3.5 (Table 2). The concentration of GGM in the TMP water was determined to be 86 to 110% after the flotation at pH 5.1, and 95 to 115% at pH 3.5 depending on the DoTAC concentration (Table 2).
At pH 3.5, about 30% of the neutral substances, 20% fatty acids, and 10% resin acids remained after flotation with 40 ppm DoTAC (Fig 5). About 20% of the neutral substances, 5% of the fatty acids, and 1% of the resin acids remained after flotation with 80 ppm DoTAC.
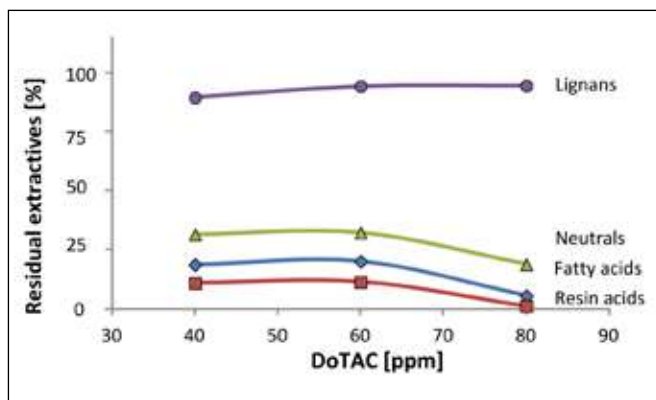
Fig 5. Residual extractives after flotation with varying DoTAC concentration at 20 °C and pH 3.5.

FLOTATION WITH DIFFERENT CONCENTRATION OF DoTAC AT 50 °C

Flotation experiments were performed with 40, 60, and 80 ppm DoTAC at 50 °C to assess the impact of a more industrially relevant temperature on the flotation. At pH 5.1, the foam volumes were 1 to 2% (Table 3). At pH 5.1, the residual turbidity of the TMP water was 50% after flotation with 40 ppm DoTAC, and the residual turbidity after flotation with 80 ppm DoTAC was 20%. The remaining pitch after the flotations at pH 5.1 was between 35 and 44% depending on the DoTAC concentration (Table 3).

Flotation	Foam volume %	Residual turbidity %	Residual pitch %	Residual uronic acids %	Residual GGM %
pH 5.1, 40 ppm	1	50	44 ± 2	102 ± 1	103 ± 1
pH 5.1, 60 ppm	2	32	35 ± 1	89 ± 3	94 ± 2
pH 5.1, 80 ppm	2	20	41 ± 0	84 ± 2	92 ± 2
pH 3.5, 40 ppm	2	29	32 ± 1	76 ± 1	89 ± 2
pH 3.5, 60 ppm	9	9	11 ± 0	86 ± 2	115 ± 1
pH 3.5, 80 ppm	22	4	8 ± 0	43 ± 1	70 ± 0

Table 3. Foam volume and residual turbidity, pitch and carbohydrates after flotation of TMP water. The experiments were conducted at pH 5.1 and 3.5 with 40, 60, and 80 ppm DoTAC at 50 °C. The deviations of the determinations are shown as ± in the table; ± 0 indicates deviation below 0.5%.

At pH 5.1, about 50% of the neutral substances, 35% of the fatty acids and 25% of the resin acids remained in the water after flotation with 40 ppm of DoTAC (Fig 6). Increasing the concentration of DoTAC from 40 to 60 ppm resulted in a further decrease in residual pitch. The most effective DoTAC concentration at pH 5.1 and 50 °C was 60 ppm, at which 45% of the neutral pitch substances, 20% fatty acids and 10% resin acids remained in the water (Fig 6), i.e. 35% of the total pitch (Table 3).
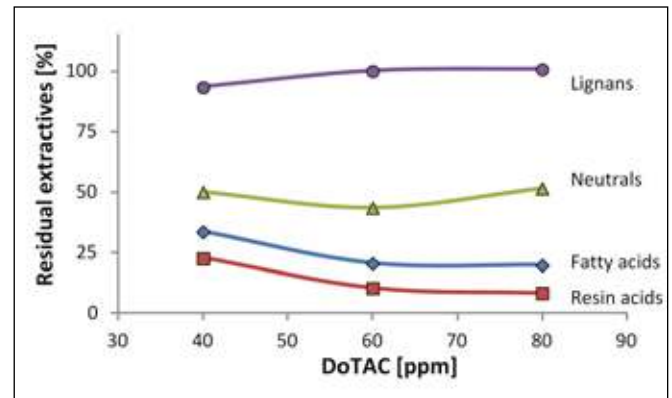
Fig 6. Residual extractives after flotation with varying DoTAC concentration at 50 °C and pH 5.1.

At pH 5.1 and 50 °C, about 102 to 84% of the uronic acids remained in the TMP water after the flotation (Table 3). The concentration of residual uronic acids decreased with increasing DoTAC concentration. The concentration of residual GGM was between 103 and 92% after the flotations, also decreasing with increasing DoTAC concentration.
Flotation experiments were also performed with varying DoTAC concentrations at pH 3.5 and 50 °C. At pH 3.5, the foam volume was 2% with 40 ppm DoTAC, while it increased significantly with increasing DoTAC concentration (Table 3). Flotation at pH 3.5 with 80 ppm DoTAC resulted in a very large foam volume, i.e. 22% of the total TMP water volume. The residual turbidity of the TMP water was 29% after flotation with 40 ppm DoTAC. Higher concentrations of DoTAC at pH 3.5 lowered the residual turbidity even further; the residual turbidity was only 9% after flotation with 60 ppm DoTAC. At pH 3.5, the total pitch concentration was about 32% after flotation with 40 ppm DoTAC, and 11% with 60 ppm. The residual concentration of uronic acids was about 76% after flotation with 40 ppm DoTAC at pH 3.5 (Table 3).
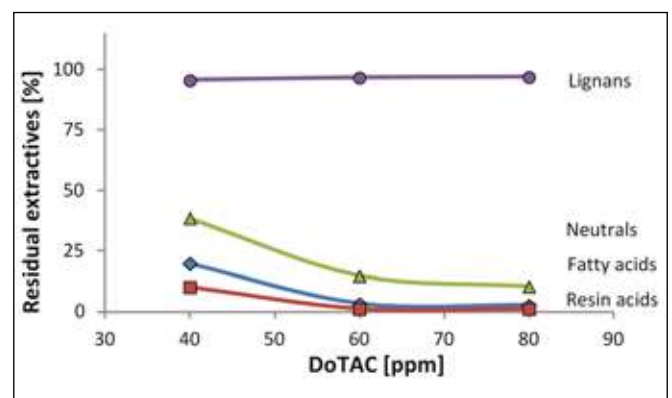
Fig 7. Residual extractives after flotation with varying DoTAC concentration at 50 °C and pH 3.5.

About 40% of the neutral substances, 20% of the fatty acids and 10% of the resin acids remained in the water after flotation with 40 ppm DoTAC (Fig 7). At pH 3.5, 15% of the neutral substances, about 5% of the fatty acids and 1% of the resin acids remained after flotation with 60 ppm DoTAC.

FLOTATION WITH ADDITIONAL AIR FLOW

Flotation experiments were performed with 60 ppm DoTAC at 50 °C, pH 5.1 for 60 min. The air flow into the flotation cell was adjusted to 9 L/min and compared to the flotation without air flow. The foam volumes were in both cases close to 2%. The residual pitch was only about 20% after flotation with 9 L/min air flow, while 35% remained after flotation without air flow at these conditions.

The residual concentration of neutral substances was 25% after flotation with 9 L/min air flow, compared to 45% without air flow (Fig 8). The residual concentration of fatty acids decreased from 20 to 10% and the residual concentration of resin acids from 10 to 5% when the air flow was used. The residual concentration of uronic acids was 90% without the air flow, while only 75% remained with the air flow. The residual concentration of GGM was only 5% lower with the air flow compared to no air flow.
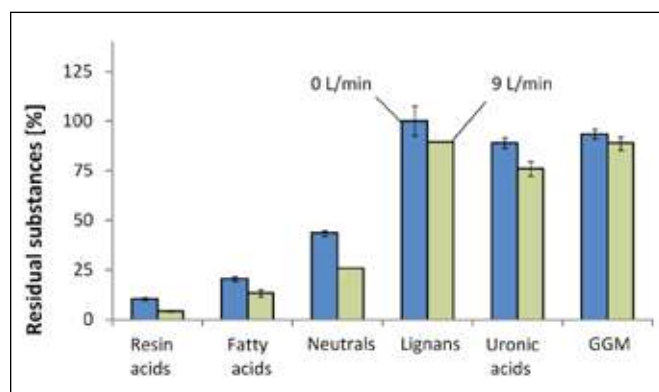

Fig 8. Residual wood components after flotation with 60 ppm DoTAC at 50 °C and pH 5.1 without air flow and with an air flow of 9 L/min. The brackets show the deviation in the determinations.

FLOTATION WITH DIFFERENT CALCIUM CONCENTRATIONS

The influence of calcium on the flotation of pitch was assessed, since calcium is omnipresent in all papermaking process waters. Flotation experiments were performed with about 0.5, 1.0 and 3.0 mM calcium at pH 5.1 for 60 min. The temperature was 20 °C and the DoTAC concentration was 80 ppm in these experiments. The lowest concentration of calcium was about 0.5 mM, which was the concentration in the received TMP water. The foam volume was 1 to 2% at all of the tested calcium concentrations, decreasing with increasing calcium concentration (Table 4). The turbidity after flotation increased slightly when the concentration of calcium increased from 0.5 to 1 mM, while increasing the concentration from 1 to 3 mM had no significant effect on the turbidity. The residual concentration of total pitch was unaffected when the calcium concentration was increased from 0.5 to 1 mM, but increased by 25% when the calcium concentration increased from 1 to 3 mM. The residual concentration of uronic acids and GGM decreased with increasing calcium concentration, and only about 60% remained after flotation with 3.0 mM calcium (Table 4).

Flotation	Foam volume %	Residual turbidity %	Residual pitch %	Residual uronic acids %	Residual GGM %
Ca²⁺ 0.5 mM	2	25	37 ± 1	101 ± 2	110 ± 3
Ca²⁺ 1.0 mM	2	33	35 ± 1	85 ± 0	92 ± 0
Ca²⁺ 3.0 mM	1	34	60 ± 1	57 ± 2	63 ± 3

Table 4. Foam volume and residual turbidity, pitch and carbohydrates after flotation of TMP water. The experiments were conducted with varying calcium concentration, 80 ppm DoTAC, at pH 5.1 and 20 °C. The deviations of the determinations are shown as ± in the table; ± 0 indicates deviation below 0.5%.

About 50% of the neutral pitch substances remained in the water after flotation at 0.5 mM calcium (Fig 9). Increasing the concentration of calcium to 1.0 mM did not have any significant effect on the removal of pitch components. Increasing the calcium concentration to 3.0 mM resulted in less efficient flotation of mainly neutral pitch components (Fig 9). The residual concentration of neutral pitch was about 75% after flotation at 3.0 mM calcium. The concentration of residual resin and fatty acids was also somewhat higher at 3.0 mM calcium, compared to at 0.5 mM and 1.0 mM calcium (Fig 9).
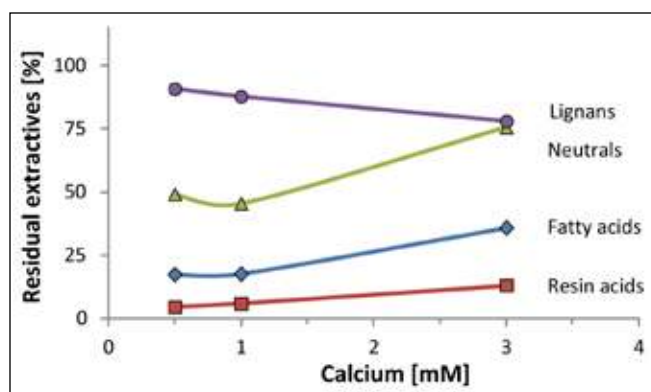

Fig 9. Residual extractives after flotation with 80 ppm DoTAC at 20 °C.

DISCUSSION

TMP waters from fresh Norway spruce normally contain more neutral pitch components than RFAs [3]. There was also a high concentration of carbohydrates in the TMP water, mainly in the form of water-soluble GGM, which provide steric stabilisation to the colloidal pitch droplets. The TMP water contained some uronic acids, as units in anionic polysaccharides, such as xylans, arabinogalactans and pectins. All of the added DoTAC concentrations in the experiments were well below the critical micelle concentration [42].

At pH 3.5, both the RFAs and the neutral pitch substances were removed to a high extent in the flotation with DoTAC. The cationic charge of DoTAC was likely to interact with the anionic charge of resin and fatty acids, leading to their removal from the TMP water. It is known from experiments on phase distribution between colloidal pitch droplets and the water phase that the RFAs are mostly attached to the colloidal droplets at pH 3 as a surface layer [12]. It is also known that the anionic

charge density of DCS from TMP is quite low at this pH due to the protonated carboxyl groups of the dissolved and colloidal substances *(15)*. Therefore, lower concentrations of a cationic coagulant are needed to achieve extensive aggregation and destabilisation of colloidal wood pitch at lower pH *(9)*. The added DoTAC probably neutralised the charges of the RFAs on the surface of the colloidal pitch droplets at pH 3.5. The neutralised pitch droplets were aggregated and removed by the flotation, which would explain why much of the neutral pitch as well as the RFAs could be removed by flotation at low pH (Fig 10). Increasing either the concentration of DoTAC or the temperature resulted in a further decrease in the residual pitch concentration in the TMP water. The large foam volumes in flotations at pH 3.5, at 50 °C and high concentration of DoTAC, showed that high DoTAC concentrations should be avoided at low pH. Excess of free DoTAC seemed to result in large foam volumes, which would be unacceptable for froth flotation in most industrial applications.

At pH 5.1, the RFAs were removed to a high extent, while the neutral pitch substances were more difficult to remove than at pH 3.5. At pH 5.1, the RFAs were not associated with the colloidal pitch droplets to the same extent as at pH 3.5, implying that some of the RFAs interacted with the DoTAC in the water phase, and not on the surface of the pitch droplets *(12)*. The neutralised RFAs were removed by the flotation, while the neutral pitch substances remained in the TMP water to a higher extent at pH 5.1 than at pH 3.5. The foam volumes in flotations at pH 5.1 were all below 2%, unlike some of the large foam volumes in flotations at pH 3.5. At pH 5.1, the carboxylic groups of the RFAs were dissociated to a high degree while the RFAs were still attached to the colloidal pitch droplets. The added DoTAC therefore targeted the colloidal pitch, which resulted in less free DoTAC in the water phase, compared to the case in the flotations at pH 3.5 (Fig 10). The lack of free DoTAC resulted in small foam volumes at pH 5.1. The results indicate that the flotation is less sensitive towards overdosing of DoTAC at pH 5.1, than at pH 3.5.

The resin acids were removed to a higher extent than the fatty acids in the flotations, indicating that the resin acids were more accessible to the added DoTAC. Phase distribution experiments have shown that resin acids are released from colloidal pitch droplets at lower pH than fatty acids *(12)*. It was recently suggested that the resin acids may form an outer shell around the colloidal pitch droplets *(43)*, shielding the carboxyl groups of the fatty acids, which could also be an explanation to why the resin acids were categorically removed more extensively than the fatty acids by this flotation setup. The removal of resin acids from process waters by flotation could be quite beneficial to the papermaking process, especially in process waters from P. radiata where resin acids are abundant *(43, 44)*. Resin acids have been specified as the major contributor to pitch deposition *(45)*. At pH 7.6, the residual concentration of RFAs in the TMP water was higher than after flotations at lower pH. The increase in pH had shifted the phase distribution of RFAs from the colloidal pitch droplets further towards the water phase *(12)*. The flotation still resulted in significant removal of RFAs, especially resin acids, from the TMP water, but the interaction between RFAs and DoTAC mainly took place in the water phase (Fig 10). The residual concentration of neutral substances was very high after the flotation, implying that little DoTAC was bound to the colloidal pitch droplets. Actually, the flotation at pH 7.6

even resulted in an increase of neutral pitch in the TMP water. This anomalous result was most likely due to release of pitch from fines at neutral conditions in combination with the hard agitation in the flotation cell. Pulp washing experiments have previously stated that more pitch is released from TMP at alkaline conditions *(2, 3, 46)*.

The foam volume was much larger at pH 7.6 compared to in the flotations at pH 5.1. This is most likely due to the high concentration of DoTAC and dissolved RFAs in the water phase at pH 7.6. It is known that dissolved RFAs are responsible for unwanted foaming in papermaking *(47)*. Neutral or alkaline conditions should be avoided during flotation, due to the extensive foaming and the low removal of neutral pitch substances.
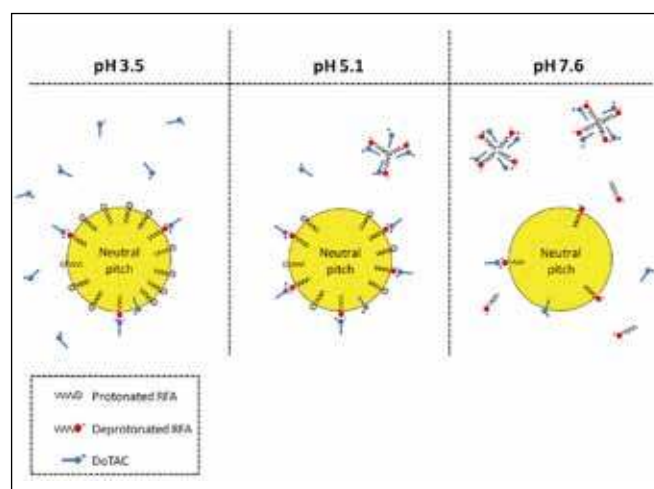

Fig 10. Proposed model of colloidal pitch, RFAs and DoTAC at different pH levels. The RFAs may have formed pre-micellar aggregates in the water phase, due to limited solubility in water. A high concentration of surface active components in the water phase will cause more foaming, which was the case at pH 3.5 and 7.6.

Both calcium and DoTAC have affinity to the anionically charged pitch and fines. Small variations in calcium concentration had no significant effect on the flotation efficiency. However, high concentrations of calcium may impair the froth flotation of pitch. Calcium ions may occupy some of the anionic sites on the colloidal pitch droplets, blocking them from interaction with DoTAC. Calcium may also form pitch aggregates that the DoTAC cannot remove, since calcium causes destabilisation and aggregation of colloidal pitch *(8, 48)*. The presence of 3 mM calcium resulted in lower efficiency of neutral pitch removal, and diminished the selectivity of the flotation, since water-soluble components, such as GGM and lignans, were also removed. Increasing the calcium concentration decreased the foam volume in the flotation, which also could explain why neutral pitch was removed less efficiently. Resin acids were removed to a high degree in the flotation, even at the highest calcium concentration. Experiments have shown that calcium soaps of resin acids are quite soluble in water, unlike calcium soaps of fatty acids. The threshold for extensive dissolution of calcium soaps of resin acids was reported to be around pH 6.5 to 7 *(14)*.

The polysaccharides containing uronic acids were not removed by the flotation with DoTAC at pH 3.5. The pectins, consisting mainly of galacturonic acid units, are methylesterified to a high

degree in unbleached TMP of Norway spruce *(49)*. The pectins are mostly uncharged and therefore not removed by flotation with DoTAC. Most of the GGM also remained in the TMP water after the flotations; the intensive agitation in the froth flotation cell even caused release of additional GGM from the fines at sufficiently high DoTAC concentration. Acetylated GGM from Norway spruce is very water-soluble before encountering alkaline conditions such as in alkaline peroxide bleaching *(17)*. The polysaccharides were extensively removed only in flotations with uncontrolled foaming at pH 3.5. Hence, flotation with DoTAC is quite selective for the removal of pitch components from TMP water.

Most of the polysaccharides, both those with uronic acids and GGM, remained in the TMP water after the flotations also at pH 5.1 and 7.6. Increasing the concentration of calcium in the flotation resulted in decreasing residual concentration of polysaccharides and lignans, i.e. the water-soluble components.

The removal of GGM might have been caused by redeposition of the hemicellulose chains onto fines in the TMP water due to the increase in conductivity. It is known that increasing ionic strength leads to a higher adsorption of hemicelluloses from unbleached TMP onto surfaces *(50)*. The decrease in concentration of uronic acids, i.e. anionic polysaccharides, may have been caused by co-aggregation with colloidal pitch. Pectins from spruce have been shown to precipitate in the presence of calcium if their molar mass is above 6 kDa *(23)*.

Higher removal of pitch and anionic polysaccharides was achieved by introduction of additional air flow into the flotation cell. The air flow introduced more air bubbles in the water during flotation, thus increasing the efficiency of pitch removal. Finding the optimal air flow, pH, DoTAC concentration and temperature is the key to achieving the best conditions for removal of colloidal pitch by DoTAC and froth flotation.

CONCLUSIONS

All pitch components are more effectively removed from TMP water by froth flotation at acidic pH compared to flotation at neutral conditions. Neutral or alkaline conditions should be avoided due to extensive foaming, release of polysaccharides such as pectins and GGM from fines, as well as low removal efficiency of neutral pitch. Resin and fatty acids are removed to a higher degree than the neutral pitch substances at all pH levels, indicating that the carboxyl groups of resin and fatty acids are targeted by the DoTAC. The anionic charge of the dissolved and colloidal substances, as well as the phase distribution of resin and fatty acids, are crucial for the flotation. The DoTAC does not aggregate and remove pectins containing uronic acids, since these are mostly uncharged prior to alkaline peroxide bleaching. High concentrations of water-soluble galactoglucomannans remain after flotation; hence this flotation setup removes pitch quite selectively.

It is evident that industrially relevant temperatures, at slightly acidic pH, optimised dosage of DoTAC and air flow are the keys to selective removal of colloidal and dissolved pitch by froth flotation.

ACKNOWLEDGEMENTS

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