

The pH-dependent phase distribution of wood pitch components in papermaking processes

Anders Strand



Laboratory of Wood and Paper Chemistry

Department of Chemical Engineering

Åbo Akademi University

Åbo 2013

Anders Strand

Born 1981, Nykarleby, Finland

M.Sc. Chemical Engineering, 2008
Åbo Akademi University, Finland

Started Ph.D. research at the Laboratory of
Wood and Paper Chemistry in 2008
Åbo Akademi University, Finland



The pH-dependent phase distribution of wood pitch components in papermaking processes

Anders Strand

Academic Dissertation

Laboratory of Wood and Paper Chemistry
Process Chemistry Centre
Department of Chemical Engineering,
Åbo Akademi University

Åbo, Finland, 2013

Supervised by:

Associate Professor Anna Sundberg
Laboratory of Wood- and Paper Chemistry
Åbo Akademi University

and

Professor Emeritus Bjarne Holmbom
Laboratory of Wood- and Paper Chemistry
Åbo Akademi University

Reviewed by:

Professor Emeritus Per Stenius
Aalto, Helsinki and Norwegian University of Science and Technology,
Norway

and

Lecturer & Research Fellow Karen Stack
School of Chemistry
University of Tasmania, Australia

Opponent:

Professor Emeritus Per Stenius
Aalto, Helsinki and Norwegian University of Science and Technology,
Norway

Custos:

Associate Professor Anna Sundberg
Laboratory of Wood and Paper Chemistry
Åbo Akademi University

ISBN 978-952-12-2943-5

Painosalama Oy – Turku, Finland 2013

TABLE OF CONTENTS

PREFACE.....	i
IMPORTANT ABBREVIATIONS AND TERMS.....	ii
ABSTRACT	iii
KEYWORDS.....	iv
SVENSK SAMMANFATTNING	v
LIST OF PUBLICATIONS	viii
CONTRIBUTION OF THE AUTHOR	ix
SUPPORTING PUBLICATIONS.....	x
1. INTRODUCTION.....	1
1.1 Objective of the work.....	2
2. REVIEW OF THE LITERATURE.....	3
2.1 Mechanical pulp	3
2.2 Wood pitch in papermaking	8
2.3 Pitch control	12
3. MATERIALS AND METHODS.....	16
3.1 Materials.....	16
3.2 Methods.....	17
3.3 Analyses.....	21
4. RESULTS AND DISCUSSION	24
4.1 Phase distribution of resin and fatty acids.....	24
4.2 Destabilisation of colloidal pitch.....	34
4.3 Flotation of TMP process water	49
5. CONCLUSIONS	57
6. REFERENCES	59

PREFACE

The work presented in this thesis has been carried out at the Laboratory of Wood and Paper Science at Åbo Akademi University under supervision of Docent Anna Sundberg and Professor (emeritus) Bjarne Holmbom. The work is part of the activities of the Process Chemistry Centre within the Finnish Centre of Excellence Programme (2006-2011) appointed by the Academy of Finland. The work has been financed by the Process Chemistry Centre, the Finnish Paper Engineers Association, and The International Doctoral Programme in Bioproducts Technology (PaPSaT).

I would like to thank Professor (emeritus) Bjarne Holmbom for igniting my interest in this field of research, my supervisor Docent Anna Sundberg for all the advice along the way, and Dr. Lari Vähäsalo for the help with various research-related things. I am grateful for the opportunity given to me by Professor Stefan Willför to complete my thesis.

I thank my past and present colleagues at the Laboratory of Wood and Paper Chemistry for all of their help. I thank my co-authors and fellow PhD students, especially Ms. Ann-Sofie Leppänen and Ms. Linda Nisula, for the support, encouragement and discussions during these years. All the help and advice received from Mr. Jarl Hemming, Mr. Leif Österholm, Docent Annika Smeds, Mr. Markku Reunanen, Docent Andrey Pranovich, and Ms. Agneta Hermansson is also gratefully acknowledged.

I would like to thank Professor Magnus Norgren and Mr. Dariusz Zasadowski for the fruitful cooperation between Åbo Akademi and Mid Sweden University.

Finally I would like to thank my family for their encouragement through the years of studies, and Marina for her support and understanding.

Åbo, September 2013

Anders Strand

IMPORTANT ABBREVIATIONS AND TERMS

4-O-Me-GlcA	4-O-methyl glucuronic acid
Ara	Arabinose
c.m.c.	Critical micelle concentration
C-PAM	Cationic polyacryl amide
DCS	Dissolved and colloidal substances
DAF	Dissolved air flotation
DoTAC	Dodecyltrimethylammonium chloride
DTPA	Diethylene triamine pentaacetic acid
FCM	Flow cytometry
FL3	Fluorescence with a wavelength of 615-645 nm
FSC	Forward scattering
Gal	Galactose
GalA	Galacturonic acid
GC	Gas chromatography
GCC	Ground calcium carbonate
GGM	Galactoglucomannan
Glc	Glucose
GlcA	Glucuronic acid
IAF	Induced air flotation
Man	Mannose
MTBE	Methyl <i>tert</i> -butyl ether
P-bl.	Peroxide-bleached
PCC	Precipitated calcium carbonate
PolyDADMAC	Polydiallyl-dimethyl ammonium chloride
RFAs	Resin and fatty acids
Rha	Rhamnose
SSC	Side scattering
TMP	Thermomechanical pulp
Unbl.	Unbleached
Xyl	Xylose

ABSTRACT

Wood contains only a very small amount of lipophilic extractives, commonly known as wood pitch. The pitch is known to cause severe problems in papermaking processes. The amount of pitch in process waters can be decreased by seasoning of the raw material prior to pulping, pulp washing, removal of pitch by flotation, adsorption of pitch onto various mineral surfaces, and retention of pitch to the fibre material by cationic polymers. The aim of this study was to determine the influence of pH on some of the methods used for pitch control.

Experiments were performed using laboratory-made wood pitch emulsions with varying pH, salt concentration, hemicellulose concentration and pitch composition. These emulsions were used to study the phase distribution of resin and fatty acids, the colloidal stability of pitch with and without steric stabilisation by galactoglucomannans, and the interactions between wood pitch and mineral particles. Purification of unbleached and peroxide-bleached mill process water was performed by froth flotation in combination with a foaming agent.

The distribution of resin and fatty acids (RFAs) between colloidal pitch droplets and the water phase was very dependent on pH. At pH 3, almost all of the RFAs were attached to the pitch droplets, while increasing the pH led to increasing concentration of dissolved RFAs in the water phase. The presence of salt shifted the release of RFAs towards higher pH, while lower ratio of neutral pitch in the emulsion resulted in release of RFAs at lower pH. It was also seen that the dissolution and adsorption of RFAs at sudden pH-changes takes place very quickly. Colloidal pitch was more stable against electrolyte-induced aggregation at higher pH, due to its higher anionic charge. The concentration of cationic polymers needed to aggregate colloidal pitch also increased with increasing pH. The surface characteristics of solid particles, such as amount of charged groups, were very important for understanding their interactions with colloidal wood pitch. Water-soluble galactoglucomannans stabilised the colloidal pitch sterically against aggregation, but could not completely prevent interactions between wood pitch and hydrophilic particles. Froth flotation of unbleached and peroxide-bleached process water showed that the pitch could be removed more effectively and selectively at low pH, compared to at neutral pH. The pitch

was removed more effectively, using lower concentrations of foaming agent, from peroxide-bleached water than from unbleached water.

The results show that pH has a major impact on various pulping and papermaking processes. It determines the anionic charge of the colloidal pitch and the solubility of certain pitch components. Because of this, the pH influences the effectiveness of pitch retention and removal of pitch. The results indicate that pitch problems could be diminished by acknowledging the importance of pH in various papermaking processes.

KEYWORDS

Thermomechanical pulp, wood resin, colloidal pitch, resin acids, fatty acids, phase distribution, pH, aggregation, flocculation, colloidal stability, deposits, galactoglucomannans, uronic acids, cationic polymers, froth flotation, induced air flotation, fillers, mineral particles, gas chromatography, flow cytometry

SVENSK SAMMANFATTNING

Granved innehåller, förutom cellulosa, hemicellulosor, pektiner och lignin, också lågmolekylära extraktivämnen, s.k. vedharts. Vedhartset utgör endast 0,5-2 % av veden och består främst av fettsyror, hartssyror, sterylestrar och triglycerider. Under framställning av mekanisk massa, frigörs största delen av vedhartset från veden till processvattnet som fett droppar av kolloidala dimensioner, även kallat kolloidalt hart. Det kolloidala hartset ackumuleras i pappersfabrikens processvatten på grund av dagens vattensystem med hög slutningsgrad. Höga koncentrationer av vedharts leder ofta till problem inom paperstillverkningen, såsom lägre styrka för det tillverkade papperet, avsättningar på maskindelar och på papperet, oönskad skumning, samt smak- och luktproblem. Problem med harts har blivit alltmer vanliga på senare år, på grund av det låga råvattenintaget och att paperstillverkningen idag alltmer sker vid neutrala eller alkaliska förhållanden.

Det finns många tillvägagångssätt för att minska harts koncentrationen i processvattnen och därmed minska hartsproblemen. Lagring av veden före massaproduktionen sänker mängden vedharts som förs in till paperstillverkningen. Andra sätt att sänka mängden vedharts i processvattnen är med hjälp av massatvätt, adsorption av harts till mineralpartiklar eller retention av harts till pappret med hjälp av katjoniska polymerer och flotation. Målet med denna studie var att undersöka hur några av dessa processer påverkas av pH.

Experiment gjordes med laboratorieframställda emulsioner av vedharts vid olika pH, där sammansättningen av vedharts komponenterna, samt koncentrationen av salt och hemicellulosor varierades. Dessa emulsioner användes för att undersöka fett- och hartssyrornas fasfördelning mellan vatten och kolloider, kolloidernas stabilitet med och utan vattenlösliga hemicellulosor och interaktioner mellan vedharts och olika mineralpartiklar. Rening av oblekt och peroxidblekt processvatten från ett pappersbruk utfördes genom flotationsexperiment med en katjonisk skumbildare.

Fett- och hartssyrorna finns i emulsionerna antingen vid ytan av de kolloidala hartsdropparna eller lösta i vattnet, beroende på pH. Fettsyror löses ut från hartsdropparna vid olika pH, beroende på deras kedjelängd och antalet dubbelbindningar i deras kolvätekedjor. Hartssyrorna löses ut från hartsdropparna vid lägre pH än fettsyror, vilket beror på att deras

ringformade kolväteskelett hindrar dem från att packas lika tätt som fettsyror. Närvaron av salt gör att fett- och hartssyror löses ut från hartsdropparna vid högre pH, medan en låg halt av neutralämnen i vedhartset gör att de löses ut vid lägre pH. Fett- och hartssyror löses ut och/eller adsorberas snabbt då pH ändras.

Interaktioner förekommer mellan lipofila hartsdroppar och hydrofila partiklar. Repulsion mellan anjoniska grupper, som bevisligen påverkas av pH och saltkoncentration, är den kraft som ger hartsdropparna kolloidal stabilitet. Sterisk stabilisering med vattenlösliga galaktoglukomannaner kan öka den kolloidala stabiliteten och därmed minska adsorptionen av vedharts på fibrer eller mineralpartiklar, men inte förhindra adsorptionen helt och hållet. Mindre doser av katjoniska polymerer behövs för aggregering av vedharts vid lägre pH. Ett lågt pH är därför att föredra i processer där effektiv aggregering av harts är av stor vikt.

Flotation av oblekt och peroxidblekt TMP processvatten, med tillsatt skumbildare, påverkas kraftigt av pH. Koncentrationen av alla vedhartskomponenter var lägre i processvattnet efter flotation vid lågt pH, jämfört med efter flotation vid neutralt pH. Effektiviteten vid flotation påverkas av mängden anjoniska laddningar på vedhartset, samt fasfördelningen av fett- och hartssyror mellan hartsdropparna och vattenfasen. Koncentrationer av vattenlösliga galaktoglukomannaner påverkades inte nämnvärt av flotation, vilket betyder att detta flotationssätt var selektivt. Resultaten visade att industriellt relevanta temperaturer, noggrant justerad pH till sura förhållanden, optimerad dos skumbildare och extra luftflöde är nyckeln till en effektiv flotation av vedharts från TMP processvatten.

Resultaten i denna avhandling visar att fasfördelningen av olika komponenter i vedharts är avgörande för ett flertal processer i papperstillverkningen. Fasfördelningen kommer att påverka massatvätt, kolloidal stabilitet, flotation och aggregering med katjoniska polymerer. En noggrann kontroll av pH samt att undvika pH chocker är av största vikt. Vissa av de hartsproblem som förekommer idag kunde undvikas med bättre pH kontroll; tvätt ska t.ex. ske vid högt pH för att öka avskiljningen av vedharts medan flotation ska ske vid lågt pH. Fixering av vedharts till fibern ska ske vid lågt pH eftersom största delen av vedhartset då kan bindas till fibrerna med en låg dos av katjoniska polymerer. Kontinuerliga pH-mätningar i vattenströmmar, kombinerat med

en effektiv pH-kontroll, är extremt viktiga för att erhålla en god körbarhet och undvika hartsproblem.

LIST OF PUBLICATIONS

This thesis is based on six original publications. Some unpublished results are also presented. The Roman numerals I-VI are used when referring to the original papers. The original publications are reproduced with the kind permission of the respective copyright holders.

- I. Sundberg, A., Strand, A., Vähäsalo, L., Holmbom, B. (2009): Phase distribution of resin and fatty acids in colloidal wood pitch emulsions at different pH-levels, *J. Disp. Sci. Technol.* 30(6), 912-919.
- II. Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B. (2011): Influence of Pitch Composition and Wood Substances on the Phase Distribution of Resin and Fatty Acids at Different pH Levels, *J. Disp. Sci. Technol.* 32(5), 702-709.
- III. Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B. (2011): Aggregation and destabilisation of colloidal wood pitch by calcium ions in TMP suspensions, *Nord. Pulp Pap. J.* 26(4), 429-437.
- IV. Strand, A., Lindqvist, H., Vähäsalo, L., Blomquist, M., Sundberg A. (2013): Analysis of interactions between colloidal wood pitch and various mineral particles by flow cytometry, *BioResources* 8(3), 3884-3900.
- V. Strand, A., Zasadowski, D., Norgren, M., Hedenström, E., Willför, S., Sundberg, A. (2012): Selective froth flotation of pitch components from spruce TMP process water, *Appita J.* 65(4), 337-346.
- VI. Zasadowski, D., Strand, A., Sundberg, A., Edlund, H., Norgren, M. (2013): Selective purification of bleached spruce TMP process water by induced air flotation (IAF), *Holzforschung*, online, (doi: 10.1515/hf-2013-0045).

CONTRIBUTION OF THE AUTHOR

The author is responsible for the experimental work and revision of the first draft of article I. The author is responsible for the experimental work and is the main author of article II. The author is responsible for the planning, experimental work and is the main author of article III and IV. The author is responsible for planning and performing the flotations in cooperation with Mid Sweden University, performing the chemical characterisation of the samples, and is the main author of article V. The author is responsible for the planning and performing the flotations in cooperation with Mid Sweden University, performing the chemical characterisation of the samples, and revision of the first draft of article VI.

SUPPORTING PUBLICATIONS

Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B. (2009): Effects of pitch composition and wood substances on the phase distribution at different pH levels, Proc. 15th International Symposium on Wood, Fiber and Pulping Chemistry, P-028, 15-18 June, Oslo, Norway.

Sundberg, A., Strand, A., Vähäsalo, L., MacNeil, D., Holmbom, B. (2009): Phase distribution in wood pitch emulsions at different pH and salt concentrations, Proc. 15th International Symposium on Wood, Fiber and Pulping Chemistry, June 15-18, Oslo, Norway.

Holmbom, B., Sundberg, A., Strand, A. (2010): Surface-active compounds as forest-industry by-products, In: "Surfactants from renewable resources", Kjellin, M., Johansson, I. (editors), Chichester, West Sussex: Wiley, 45-62.

Strand, A., Sundberg, A., Vähäsalo, L., Holmbom, B. (2011): Destabilization of colloidal wood pitch by calcium ions in TMP suspensions, Proc. 16th International Symposium on Wood, Fiber and Pulping Chemistry, June 8-10th, Tianjin, China.

Strand, A., Sundberg, A., Lu, X., Vähäsalo, L. (2011): Effect of metal ions and wood pitch on paper properties, Proc. 16th International Symposium on Wood, Fiber and Pulping Chemistry, June 8-10th, Tianjin, China.

Honorato, C., Strand, A., Vähäsalo, L., Sundberg, A. (2012): Effect of cationic polymers and aluminium sulphate on pitch from spruce TMP, Report C1-2012.

Strand, A., Zasadowski, D., Norgren, M., Hedenström, E., Willför, S., Sundberg, A. (2013): Selective froth flotation of pitch components from spruce TMP process water, Proc. 17th International Symposium on Wood, Fiber and Pulping Chemistry, June 12-14th, Vancouver, Canada.

Zasadowski, D., Strand, A., Sundberg, A., Willför, S., Edlund, H., Hedenström, E., Norgren, M. (2013): Selective flotation – Key for chemical recovery and better production processes, Proc. 17th International Symposium on Wood, Fiber and Pulping Chemistry, June 12-14th, Vancouver, Canada.

1. INTRODUCTION

Wood contains only a very small amount of lipophilic extractives, commonly known as wood pitch. Even though the pitch is a minor component, its detrimental effects on the papermaking process can be quite profound. Pitch can cause lowered tensile strength of the produced paper, formation of deposits on paper machine parts and felts, unwanted foaming, spots and holes in the paper, and problems with odour and taste (see e.g. Allen 2000). Pitch problems have become more prominent in recent years, due to a higher degree of closure of the water systems, and the increasing popularity of neutral and alkaline papermaking processes. The severe impact of pitch on papermaking can be directly seen in the number of actions that have been applied to diminish pitch problems. The amount of pitch in process waters can be decreased by seasoning of the raw material prior to pulping, pulp washing, removal of pitch by flotation, adsorption of pitch onto various mineral surfaces, and retention of pitch to the fibre material by cationic polymers (see e.g. Tanase-Opedal et al. 2011a). Effective pitch control is a very important part of ensuring a good runnability of a paper machine.

The topic of wood pitch in papermaking has therefore been studied extensively throughout the years, using water containing dissolved and colloidal substances released from thermomechanical pulp or process water from paper mills. These waters are complex mixtures of lipophilic and hydrophilic components, which have made the interpretation of mechanisms quite difficult in many cases. Laboratory-made pitch emulsions can be used in small scale studies in order to focus on the colloidal wood pitch, and to minimise the influence of hydrophilic components or additives on the results. More basic studies of pitch interactions are needed in order to fully understand its behaviour in different stages of the papermaking process.

The pH in papermaking is ever changing; mechanical pulping takes place at slightly acidic pH, peroxide bleaching is performed at alkaline pH, and the papermaking process is nowadays mostly done at neutral or slightly alkaline pH. Additionally, combination of water streams with different pH may cause sudden changes in local pH conditions in the process. The pH-dependent properties of wood pitch, especially of colloidal wood pitch, are therefore extremely relevant to most papermaking processes. Pitch problems could be

diminished by acknowledging the importance of pH and better understanding the behaviour of pitch.

1.1 Objective of the work

This study focuses on the effects of pH on different papermaking processes. The main objective was to determine the pH-dependent phase distribution of resin and fatty acids in wood pitch emulsions, and how this affects the colloidal stability and sorption of pitch. Laboratory-made pitch emulsions were used in order to focus on the behaviour of pitch at carefully controlled conditions. Additionally, selective removal of pitch by froth flotation was assessed.

2. REVIEW OF THE LITERATURE

2.1 Mechanical pulp

Norway spruce (*Picea abies*) wood is a natural composite, which consists of 42-47% cellulose, 24-28% hemicelluloses and pectins, 27-32% lignin and 0.5-2% extractives (Sjöström 1981; Kappel 1999; Bertaud, Holmbom 2004). In the Nordic countries, Norway spruce is commonly used as a raw material for mechanical pulps. In mechanical pulping, the wood raw material is defibrated into pulp suitable for papermaking by applying mechanical energy (Sundholm 1999). The defibration can take place at atmospheric pressure by grinding to produce groundwood pulp (GW), or by refining to produce refiner mechanical pulp (RMP) (Kappel 1999). There is a large variety of mechanical pulps, depending on whether the wood is subjected to grinding or refining, whether the defibration is performed at atmospheric pressure or at pressurised conditions, and whether the wood has been subjected to any pre-treatment prior to defibration (Kappel 1999; Sundholm 1999). When wood chips are preheated and refined under pressure at temperatures exceeding 100°C, the resulting pulp is known as thermomechanical pulp (TMP).

2.1.1 Mechanical pulp fibres and fines

The defibration in mechanical pulping is not uniform, and mechanical pulps therefore consist of fibres, fibre fragments and fines (Fig 2.1) (Höglund 2009). Different cell wall layers, such as the middle lamella, primary and secondary wall, are exposed on the fibres after the pulping procedure. Much of the surfaces of TMP fibres and fines therefore consist of lignin and extractives (Kangas, Kleen 2004). TMP fines contain a lot of pectins, since pectins are mainly located in the middle lamella, which is exposed during pulping (Mosbye et al. 2002; Sundberg, A. et al. 2003). The anionic charges of mechanical fibres and fines originate mainly from the carboxyl groups of uronic acids (Holmbom et al. 2000).

Freshly produced TMP is yellowish to brown, with an ISO brightness of about 60-63, and bleaching is needed prior to papermaking (Gellerstedt 2009). Alkaline peroxide bleaching of mechanical pulps is quite common, since it can increase the ISO brightness of the pulp to about 80 with low yield losses. The increased brightness is caused by elimination of chromophoric groups in the lignin part of the TMP. However, alkaline treatment of mechanical pulps

also leads to other reactions, such as the formation of free carboxyl groups due to demethylation of pectins (Sundberg, A. et al. 1999; Holmbom et al. 2000; Fardim et al. 2002; Pranovich et al. 2003; Gellerstedt 2009). Therefore, the anionic charge of peroxide- bleached TMP is higher than the anionic charge of unbleached TMP.

The wide size distribution of the pulp components, combined with their lignin rich nature and high stiffness of the fibres, give the mechanical pulps their unique character. Besides a yield of 97-98%; high opacity and high fibre stiffness are the two main advantages with using mechanical pulps in paper production (Sundholm 1999; Höglund 2009). Mechanical pulps are mainly used for applications such as newspaper, where the production is mass-produced, the life time expectancy is short, and the brightness and strength requirements are moderate (Kappel 1999; Höglund 2009).

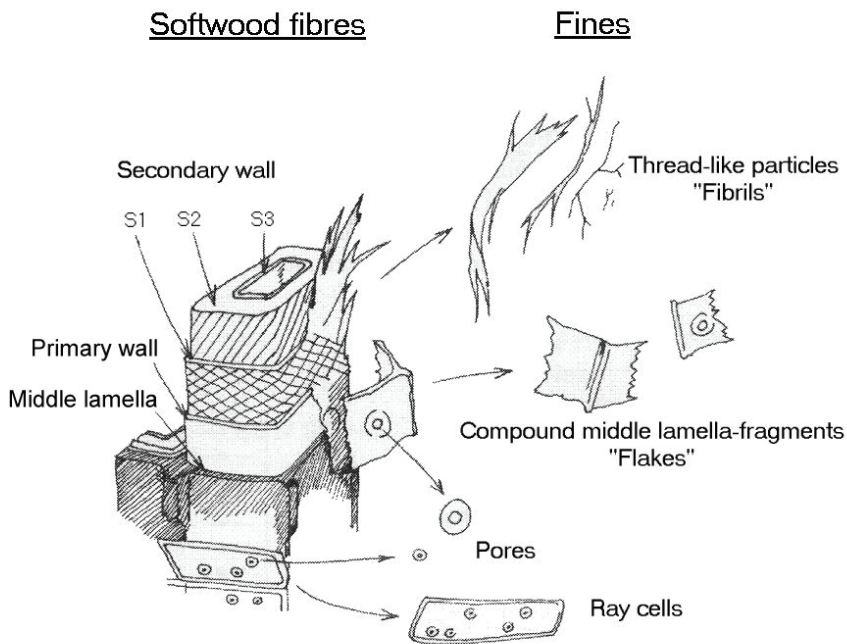


Fig 2.1 A schematic of the different fractions in a mechanical pulp (Rundlöf 2002).

2.1.2 Dissolved and colloidal substances from wood

Various wood components are released into the process water, as dissolved or colloidal substances, during production of thermomechanical pulp (TMP) and wood-containing paper (Allen 1975; Örså et al. 1997; Sundberg, K. et al. 1994a; Pranovich et al. 2005). These are mainly polysaccharides, lignin fragments, extractives and inorganic salts.

Lipophilic extractives

Extractives are low-molar-mass components that can be extracted from wood with solvents. Fatty acids, resin acids, steryl esters, sterols, and triglycerides, all belong to the class of lipophilic extractives (Sjöström 1981). Mixtures of lipophilic components are commonly called wood pitch, or wood resin. The wood pitch in TMP suspensions can be smeared onto fibre surfaces, can reside inside parenchyma cells, or be suspended in the water as colloidal droplets (Allen 1975; 1980; Fengel, Wegener 1984; Ekman et al. 1990; Koljonen et al. 2003).

The resin acids found in Norway spruce are tricyclic compounds of abietane or pimarane type, originally found inside the resin canals (Fengel, Wegener 1984; Ekman, Holmbom 2000). The pimarane type of resin acids has methyl and vinyl groups at the C-13 position (Fig 2.2). Resin acids of abietane type have an isopropyl or isoprenyl group at this position and their double bonds are conjugated. A special resin acid is dehydroabietic acid, which contains an aromatic ring in its structure. The dominating resin acid in spruce is normally dehydroabietic acid (Fengel, Wegener 1984; Björklund Jansson, Nilvebrant 2009). The fatty acids found in softwood are usually unbranched, consisting of 16-24 carbon atoms (Sjöström 1981; Fengel, Wegener 1984). The dominating species in Norway spruce are mono-, di- and tri-unsaturated fatty acids with 18 carbon atoms (Fig 2.2) (Ekman, Holmbom 2000; Björklund Jansson, Nilvebrant 2009). The fatty acids are mainly located within the parenchyma cells of the living tree.

Most of the fatty acids in spruce are found in esterified form with glycerol, forming e.g. triglycerides (Sjöström 1981; Fengel, Wegener 1984; Ekman, Holmbom 2000). Triglycerides are more common than di- and monoglycerides. The fatty acids found in the triglycerides are mainly of the same type as the ones found in free form, i.e. mainly unsaturated fatty acids

such as oleic and linoleic acid (Fig 2.2). The fatty acids are also found esterified with sterols, forming steryl esters. Both triglycerides and steryl esters are very hydrophobic, and insoluble in water.

In alkaline peroxide-bleaching only minor changes occur in the lipophilic extractives (Holmbom 2000). Peroxide reacts mainly with conjugated double bonds and causes oxidation of resin acids like abietic, palustric, levopimaric, and neoabietic acid. Only slight changes occur in the fatty acids. Alkaline peroxide bleaching does not cause significant hydrolysis of triglycerides or steryl esters.

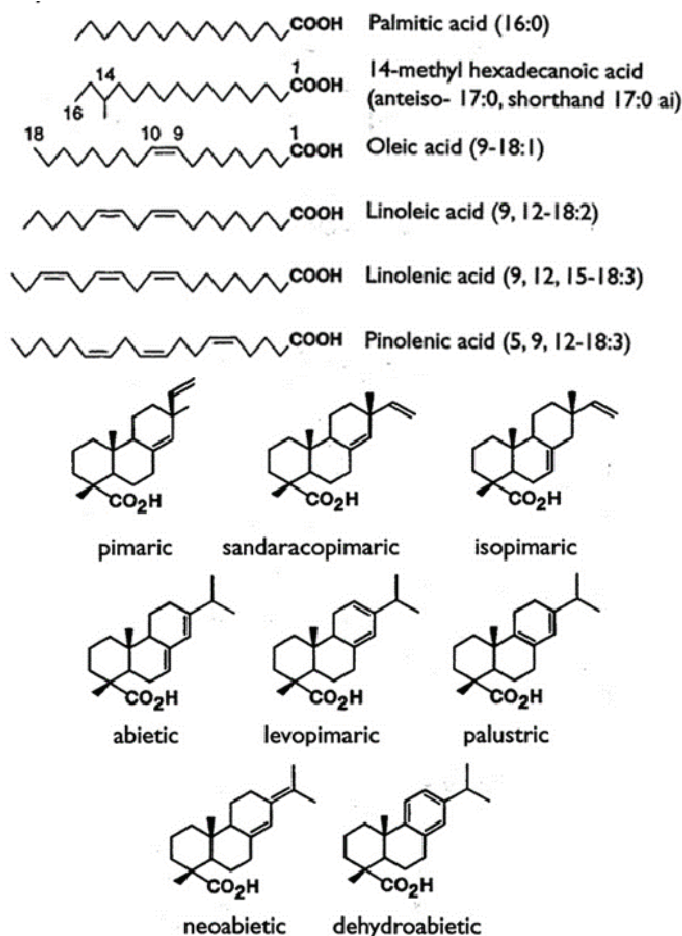


Figure 2.2 Common resin and fatty acids found in softwood (Modified from Ekman, Holmbom 2000).

Hemicelluloses and pectins

The main hemicelluloses found in Norway spruce are galactoglucomannans (GGM) (Sjöström 1981; Fengel, Wegener 1984). These consist of a backbone of (1→4) linked β -D-glucopyranose and β -D-mannopyranose units. The backbone of the GGM contains acetyl groups on the C2 and C3 of mannose units, as well as side groups consisting of (1→6) linked α -D-galactopyranose units (Fengel, Wegener 1984; Stenius 2000). Acetylated GGM is readily soluble in water. However, alkaline conditions, such as those found in alkaline peroxide bleaching, render the GGM less soluble in water due to deacetylation (Thornton et al. 1994).

Pectins isolated from wood are composed of a backbone of α -(1→4)-linked galacturonic acid units, with some rhamnose units that are linked with α -(1→2) and α -(1→4)-bonds to adjacent galacturonic acid units (Fengel, Wegener 1984). The carboxyl groups of the galacturonic acid units are mostly methylated in native wood pectin; the degree of methylation in spruce wood is about 0.78 (Pranovich et al. 2002). Methylated pectins are therefore mostly uncharged. However, demethylation reactions occur at alkaline conditions, such as in peroxide bleaching, leading to the formation of free carboxyl groups (Holmbom et al. 2000; Pranovich et al. 2003). Demethylation of pectins is the main reason why the anionic charge of mechanical pulp increases during peroxide bleaching, or even during alkaline treatment without peroxide (Sundberg, A. et al. 2000; Fardim et al. 2002).

Inorganic components

Wood material contains varying amounts of inorganic components; the dominating metal ions are alkali and alkali earth metal ions such as potassium, calcium and magnesium (Fengel, Wegener 1983; Stenius 2000; Werkelin et al. 2005; Granholm 2011). The inorganic substances can be present in the tree as salt deposits in cell walls or bound to the carboxyl groups of wood components, such as in pectins or xylans. The metal ions may be released from the wood matrix during pulping. However, all of the metal ions present in process water do not originate from the wood raw material. Other sources of metal ions are e.g. the raw water, the fillers used, streams from the deinking process, and chemical additions in the bleaching stage (Neimo 1999; Stenius 2000; Werkelin et al. 2005; Granholm 2011).

2.2 Wood pitch in papermaking

The amount of wood pitch in wood is very low, but the impact it has on the papermaking process is quite large (Allen 2000). Wood pitch in papermaking is usually linked with various detrimental effects, such as lowered tensile strength of the produced paper, unwanted foaming in the process, formation of deposits on the paper and on machine parts and felts, and problems with odour and taste (Allen 2000). It is important to understand the origins of the different pitch problems in order to solve them, or in order to avoid them. The most detrimental type of pitch in papermaking is known as colloidal wood pitch (Allen 1975); about 80% of the total wood pitch enters the paper machine in colloidal form. Closure of the water system in paper mills causes accumulation of colloidal pitch, and uncontrolled aggregation of colloidal pitch is commonly linked to process disturbances such as formation of deposits and overall runnability problems (Allen 1975; Hassler 1988; Ekman et al. 1990; Nylund et al. 1993; Back 2000; Mosbye et al. 2008).

2.2.1 Resin and fatty acids in water

The resin and fatty acids (RFAs) are surface active, since they contain a hydrophobic carbon skeleton, as well as a hydrophilic carboxyl group (Fig 2.2) (Ödberg et al. 1985; Ström et al. 1990; Ström 2000). A carboxylic acid (RCOOH) in water may donate its proton to the surrounding water, forming a hydronium ion (H_3O^+) and its conjugate base (RCOO^-) (Fox, Whitesell 1997). The acidity constant (K_a) describes the proton-donating ability of an acid. The pH where 50% of the acids proton-donating groups are protonated and 50% dissociated is described by $-\log K_a$, also known as $\text{p}K_a$. The reported $\text{p}K_a$ of RFAs are in the range of 5.0-6.4 (Ström 2000), meaning that they are weak acids.

It has been shown that the apparent $\text{p}K_a$ of fatty acids in a surface layer increases with increasing chain length, due to molecular cooperativity introduced by van der Waals interactions, and ion-dipole interactions between the carboxyl groups (Kanicky et al. 2000; Kanicky, Shah 2002; 2003). Because of the cooperativity between fatty acids adsorbed at the air/water interface, the observed $\text{p}K_a$ of stearic acid (18:0) may therefore be as high as 10.15. Double bonds introduce a 70° bend in the fatty acid chain. This has been shown to lower the $\text{p}K_a$ of the fatty acid; the intermolecular distance in a surface layer increases because a larger space is required for one fatty acid

chain to rotate and the intermolecular cooperativity diminishes because of this (Fig 2.3) (Kanicky, Shah 2002). It was also shown that the observed pK_a of long-chained fatty acids decreased with decreasing concentration; because of this it was concluded that pre-micellar aggregates of fatty acids in solution are responsible for increasing the observed pK_a (Kanicky, Shah 2003). Foam height, foam stability and bubble lifetime of fatty acids soaps were shown to be at an optimum at pH near the measured pK_a of the acids. This indicated that the packing of fatty acid molecules was closest at their pK_a , through ion-dipole interactions among the carboxyl groups of the acids (Kanicky et al. 2000; Kanicky, Shah 2002).

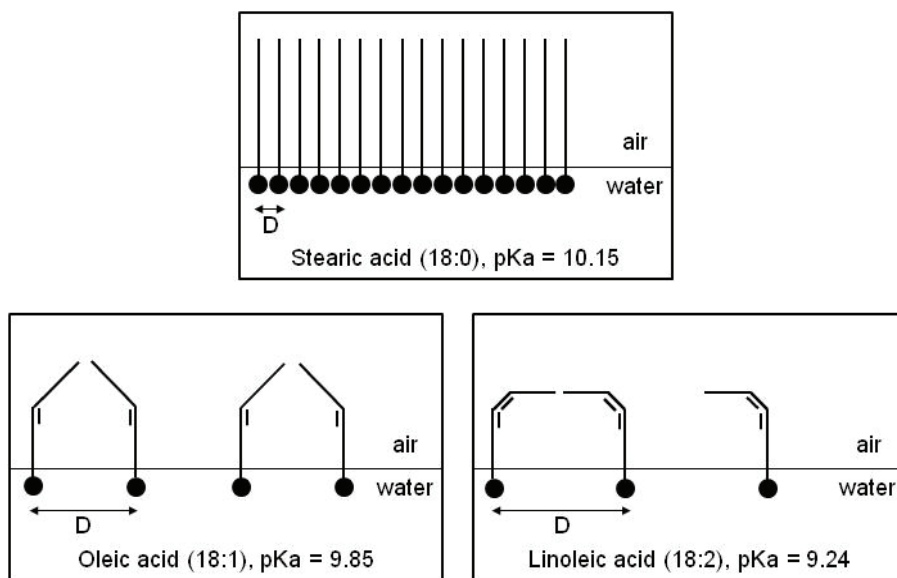


Figure 2.3 An illustration of fatty acids with varying amount of double bonds in monolayers at the water-air interface (Modified from Kanicky, Shah 2002). The intermolecular distance (D) increases when double bonds are introduced in the hydrocarbon chain.

The observed pK_a of the tested fatty acids tended to level off at concentrations above their critical micelle concentration (c.m.c.) (Kanicky, Shah 2003). Therefore, pK_a -values of RFAs determined by titration above their respective c.m.c. have been termed colloidal pK_a (McLean et al. 2005a). The colloidal pK_a -values of saturated fatty acids increases with increasing chain length, and decreases for every double bond introduced in the hydrocarbon chain. The colloidal pK_a of the tested resin acids was 6.8 to 7.3 at 20°C, but at 50°C the

determined values were 6.2 for all resin acids. Protonated RFAs have very low solubility in water (Ström 2000), however, dissociated RFAs will dissolve in water as metal soaps if the pH is above their pK_a (Heikkilä et al. 1970). The formation of water-insoluble metal soaps of RFAs, usually with Ca^{2+} , Mg^{2+} or Ba^{2+} , depended on the availability of soap anions, i.e. is also dependent on pH (Allen 1988). The surface-active and pH-dependent properties of lipophilic extractives have been investigated previously (Palonen et al. 1982; Ödberg et al. 1985; Kanicky et al. 2000; Kanicky, Shah 2003; McLean et al. 2005b).

2.2.2 Colloidal wood pitch

The papermaking furnish consists of particles of colloidal dimensions (Scott 1996). It usually consists of particles such as colloidal wood pitch ($< 1 \mu m$), fines ($1-2 \mu m$), and fillers ($0.1-10 \mu m$), while the fibres themselves fall outside this range (Eklund, Lindström 1991). Colloidal systems are metastable, and may be susceptible to flocculation or coagulation (Lindström 1991). Electrostatic stabilisation of colloids is caused by the repulsion between particles carrying similar charge, while steric stabilisation relies on polymers to sterically prevent aggregation of particles.

Wood pitch forms colloidal droplets in water due to its low solubility. The core of these pitch droplets consists of the most hydrophobic extractives, that is, triglycerides and sterol esters (Qin et al. 2003; Vercoe 2004). Surface-active RFAs are enriched as a layer on the surface, with their carboxyl groups oriented towards the surrounding water, stabilising the colloids electrostatically. This is in agreement with the fact that protonated acids tend to be attached to available surfaces due to low solubility in water (Kanicky et al. 2000; Ström 2000; Björklund Jansson, Nilvebrant 2009). The original pitch model by Qin and co-workers (2003) states that resin and fatty acids are enriched at the surface of the pitch droplets, and the model does not differentiate between the two types of acids (Fig 2.4a). More recent studies have shown that the resin acids may form an outer layer around the fatty acids and the neutral pitch, if the ratio of neutral pitch to resin and fatty acids is low (Fig 2.4b) (Lee 2011; Richardson et al. 2012). The surface layer of the colloid determines its stability, charge, and deposition tendencies. The influence of variables, such as pH and electrolyte concentration, on the behaviour of colloidal pitch, is important for papermakers.

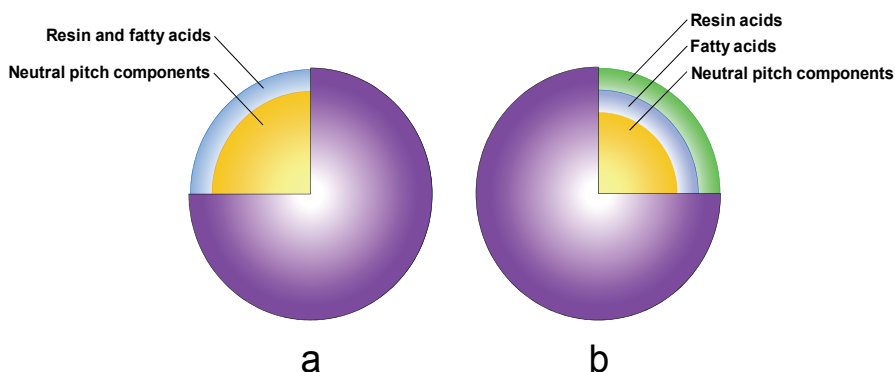


Figure 2.4 Two proposed models of colloidal wood pitch according to a) Qin et al. 2003; Vercoe 2004 at high ratios of neutral pitch to RFAs, and b) Lee 2011; Richardson et al. 2012 at low ratios of neutral pitch to RFAs.

The pitch colloids have been shown to carry an anionic charge at pH above 3, due to de-protonated carboxyl groups of RFAs (Sundberg, K. et al. 1996b; Nylund et al. 2007). The anionic charge provides electrostatic stability to the pitch. 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 (Sundberg, K. et al. 1996b). The stability of pitch emulsions from TMP against electrolyte-induced aggregation and the deposition tendencies of pitch in different chemical environments have been investigated extensively (see e.g. Back 2000). The large number of substances and varying electrolyte concentrations in process waters makes it difficult to understand the role of the individual pitch components, and the determined pK_a -values and colloidal pK_a -values for RFAs do not contain enough information to explain the behaviour of RFAs in process waters (Kanicky, Shah 2003; McLean et al. 2005a).

The colloidal pitch droplets in paper mill process waters are not only electrostatically stabilised, but may also be sterically stabilised against electrolyte-induced aggregation by water-soluble hemicelluloses, and water-soluble lignin fragments (Lindström et al. 1988; Welkener et al. 1993; Sundberg K. et al. 1994a; 1994b; Sihvonen et al. 1998; Nylund et al. 2007). Total aggregation of colloidal wood pitch by addition of calcium chloride was rendered impossible by addition of water-soluble hemicelluloses (Sundberg, K. et al. 1994a; 1994b). Water-soluble hemicelluloses released from Norway spruce during mechanical pulping, especially galactoglucomannans (GGM),

have been shown to sterically stabilise colloidal pitch droplets (Welkener et al. 1993; Sundberg, K. et al. 1994a; Hannuksela, Holmbom 2004; Johnsen et al. 2004; Tanase-Opedal et al. 2011a). 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 (Sundberg, K. et al. 1996a; Thornton et al. 1994). A high concentration of water-soluble GGM is generally considered beneficial in order to avoid deposition problems, and improve the runnability of a paper machine.

2.3 Pitch control

Pitch control is needed in papermaking, since various pitch problems would otherwise be too prominent (2.2). Dissolved anionic carbohydrates, as well as colloidal pitch, are also considered to be 'anionic trash' in papermaking since they consume expensive retention chemicals (Dunham et al. 2000). 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 mineral particles, passivation of the colloidal pitch by treatment with protein based detackifier, or removing these substances from the process waters by ultrafiltration or flotation (Sundberg, A. et al. 1994; Allen 2000; Gantenbein et al. 2010; Haapala et al. 2010; McLean et al. 2010; Tanase-Opedal et al. 2011).

2.3.1 Seasonal variations, seasoning and enzymatic treatment

The wood can be stored as chips or logs prior to pulping to decrease the amount of wood resin; this is known as seasoning. The main reactions taking place during the seasoning are oxidation of wood resin, and hydrolysis of esterified components by microbial degradation (Ekman 2000; Björklund Jansson, Nilvebrant 2009). The concentrations of lipophilic components in mill process waters also undergo seasonal variations (Ekman 2000; Holmbom et al. 2004). The variation takes place due to higher levels of hydrolysis of triglycerides into free fatty acids during the warm part of the year. The ratio of esterified pitch to RFAs in mill process waters is therefore considerably lower in the summer months than in the winter months. The amount of triglycerides in the raw material can be decreased further by biological

treatment with fungi or enzymes (Sjöström 1981; Ekman 2000). Lipases are used to cleave fatty acids from triglycerides and steryl esters (Teeri, Henriksson 2009).

2.3.2 Aggregation and retention

Cationic polymers are often used in papermaking to control dissolved and colloidal substances, which would otherwise accumulate in the process water and cause problems with runnability (Wågberg, Åsell 1995). The cationic charges of the polymers interact with the anionic charges of the colloidal pitch, and aggregation occurs by charge neutralisation, patch flocculation or bridging flocculation (Eklund, Lindström 1991; Scott 1996). The effectiveness of polymers for flocculating DCS has been previously investigated by the use of different polymers with different molar masses and charge densities (Sundberg, A. et al. 1994; Nurmi et al. 2004; 2006).

2.3.3 Adsorption to minerals

Fillers and additives, such as kaolin, bentonite, talc, ground calcium carbonate (GCC), and precipitated calcium carbonate (PCC), are currently widely used in papermaking applications. Fillers are added to the paper furnish to replace a portion of the fibres with a less expensive material or to improve e.g. the printability, opacity and whiteness of the produced paper (Eklund, Lindström 1991). Mineral particles, such as bentonite and talc, are also commonly used for adsorption of “anionic trash”. Kaolinites and bentonites are flake-like particles consisting of layered crystalline structures (van Olphen 1955; Solomon, Hawthorne 1983a). The flake-like particles are amphoteric because they develop cationic charges along their edges and anionic charges on their basal surfaces in neutral or weakly acidic media (Eklund, Lindström 1991). PCC and GCC are naturally cationic, but can be anionic at papermaking conditions, due to excess of carbonate ions, adsorption of anionic impurities or possible additions of anionic dispersing agents.

Some studies have previously focused on the interactions between wood pitch components and mineral surfaces. Adsorption experiments with oleic acid, a fatty acid, and triolein, a triglyceride, onto various mineral surfaces, showed that the mineral surface type and surface treatment of the mineral both played a major role in adsorption (Rogan 1994). Adsorption studies of oleic acid and abietic acid and DCS from peroxide-bleached TMP onto PCC and

talc pigments have shown that PCC does adsorb both oleic and abietic acid, until the cationic charge of the PCC is neutralised (Miyanishi et al. 2000). Interactions between different minerals and DCS from spruce have also been studied by mixing peroxide-bleached or unbleached TMP water with mineral particles (Willför et al. 2000). It was seen that additions of kaolin removed some pitch, GGM, and pectins from unbleached and peroxide-bleached TMP water at pH 5 and 8. PCC adsorbed pitch more selectively than kaolin, i.e. most of the water-soluble GGM remained in the water after the adsorption experiments. Adsorption experiments with DCS onto talc, magnesium aluminium silicate, and kaolin particles have shown that more pitch was removed when more mineral particles were added, independent of which filler was added (Mosbye et al. 2003). It was also seen that less pitch was removed when dissolved substances from spruce were added in the experiments, i.e. mainly GGM. Adsorption experiments with unbleached DCS onto GCC, surface modified GCC, and talc have shown that very high concentrations of native GCC were needed in order to achieve significant pitch removal (Gantenbein et al. 2012).

2.3.4 Removal by flotation

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 (Tanase-Opedal et al. 2011a; 2011b; Richardson, Grubb 2004; Negro et al. 2005; Saarimaa et al. 2006a; 2006b). 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* (Richardson, Grubb 2000). Removal of colloidal pitch from peroxide-bleached TMP water from Norway spruce by PAC, polyacrylamide (PAM) /bentonite or PEO/PFR and subsequent DAF treatment has been shown to be quite effective (Saarimaa et al. 2006a). DAF experiments with added cationic polyacrylamide (C-PAM) and polydiallyldimethylammonium chloride (polyDADMAC) successfully removed about 70% of the total pitch from pressate samples from Norway spruce chips (Tanase-Opedal et al. 2011b). However, about 60% of the hemicelluloses were also removed by the DAF treatment. It has been reported that substantial amounts of pitch could be removed by DAF treatment from *Pinus radiata* newsprint process waters even without addition of chemicals (Richardson, Grubb 2000). However,

dissolved pitch components, i.e. mainly resin acids, are difficult to remove from the waters by flocculation and subsequent DAF treatment (Richardson, Grubb 2000; Saarimaa et al. 2006a; Tanase-Opedal et al. 2011a). The efficiency of the RFA-removal with DAF is strongly affected by pH. The chemical composition, the mechanisms of the flotation, and the dose of the used additives dictate the optimal flotation conditions (Sundberg, A. et al. 1994; Richardson, Grubb 2000; Saarimaa et al. 2006a).

Froth flotation, or induced air flotation (IAF), was recently suggested for removal of pitch and manganese from TMP waters (Zasadowski et al. 2012a; 2012b) or directly from diluted mechanical pulps with added calcium (Korpela 2006). Froth flotation of TMP water in combination with various foaming agents was assessed (Zasadowski et al. 2012b). It was seen that additions of dodecyltrimethylammonium chloride (DoTAC) lead to a lower residual turbidity than the other tested foaming agents. Froth flotation is commonly used in deinking flotation and an advantage of this flotation setup could possibly be lower material losses than in DAF (Costa, Rubio 2005).

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Thermomechanical pulp (TMP) (I-IV)

TMP was obtained from a mill in Finland using two-stage refining of Norway spruce (*Picea abies*). The pulp consistency was about 40%, and the pulp was stored at -18°C until used.

3.1.2 Model pitch components (I; II)

Palmitic acid (16:0), stearic acid (18:0), and oleic acid (18:1) were extracted from a commercial soap (Raisapon 105, Ciba Specialty Chemicals, Switzerland) (I; II). Linoleic acid (18:2) was obtained from Sigma (USA), oleic acid (18:1) from Fluka (Switzerland), arachidic acid (20:0) from Fluka (Switzerland), behenic acid (22:0) from Sigma (USA), and lignoceric acid (24:0) from Fluka (Switzerland). A mixture of resin acids was obtained by extraction of solid oleoresin from Norway spruce with hexane (II). Triglycerides, in the form of soybean oil, were obtained from Oilio (Belgium).

3.1.3 Galactoglucomannans (GGM) (II-IV)

GGM was isolated at a Finnish paper mill producing thermomechanical pulp from spruce. The GGM was isolated from the effluent by different filtration techniques and was then spray-dried (Xu 2008).

3.1.4 Mineral particles (IV)

Prismatic precipitated calcium carbonate (PCC), Albaglos S, was received from Specialty Minerals Inc., New York, USA. The prismatic PCC was received as slurry with a high dry content, containing anionic dispersing agent. Scalenohedral PCC, Velacarb, was received from Specialty Minerals Nordic OY, Anjalankoski, Finland. The ground calcium carbonate (GCC) was a commercially available GCC. Kaolin, Intramax JR, was received from Imerys Minerals Ltd, Par Cornwall, UK. Three different bentonite samples, Pitchbent K, Pitchbent UF and EXM 1694, were received from Clariant Produkte GmbH, Moosburg, Germany. All of the minerals were used without further purification.

3.2 Methods

3.2.1 Pitch emulsions from spruce extract (I; III; IV)

The pitch emulsion was prepared according to the method described by Sundberg K. and co-workers (1996). TMP was freeze-dried and extracted with n-hexane. The hexane evaporated, and the pitch was re-dissolved in acetone to a concentration of 30 mg/mL. Wood pitch in acetone was injected into distilled water under agitation, to a pitch concentration of about 500 mg/L (Fig 3.1a). The acetone in the emulsion was then removed by dialysis. The concentration of pitch in the emulsion was adjusted to about 200 mg/L with distilled water. In some cases, saturated fatty acids were added to the wood pitch acetone-solution prior to the injection into distilled water (Fig 3.1b).

3.2.2 Pitch emulsions from model components (II)

Pitch emulsions were also prepared from model components. Acetone solutions of fatty acids, resin acids and triglycerides were mixed together in different ratios (Fig 3.1c). The pitch in acetone was injected into distilled water and dialysed according to the procedure described in 3.2.1. The pitch emulsion was diluted with distilled water, or GGM-solution, to a pitch concentration of about 110 mg/L.

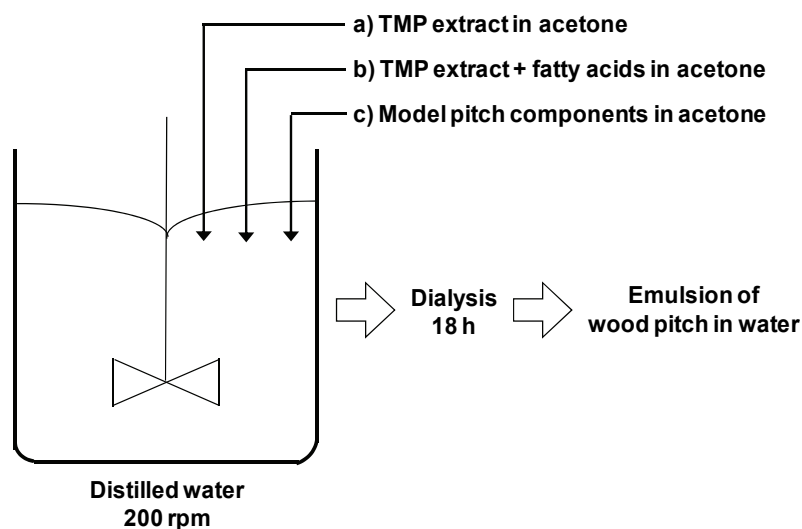


Fig 3.1 Preparation of pitch emulsions from different starting materials.

3.2.3 Phase distribution experiments (I; II)

The pH of the emulsion was adjusted with dilute H₂SO₄ or NaOH. The emulsion was then heated to 30, 50, or 70°C and agitated for 3 hours. Samples of the emulsion were filtered through 0.2-µm (Titan 2, HPLC filter purple nylon membrane) or 0.1-µm (Whatman, Anotop 25 Plus, 25 mm, inorganic membrane) syringe filters. To ensure that no neutral pitch would pass through the filter, syringe filters with 0.1 µm pores were used for pitch emulsions with low concentration of neutral pitch. The concentration of resin and fatty acids in the filtrate were determined by GC and compared to the concentration in the unfiltered emulsion. The experimental distribution data were used to fit a sigmoid curve (Janowsky et al. 1999), extending from 0 to 100% (Eq 1). It is possible to define a sigmoid such that it can be fitted to experimental data by adjusting two independent constants; in this case the pK_{lw} and the slope of the curve (I). The pK_{lw} represents the pH where 50% of the component in question is dissolved. P represents the maximum concentration of dissolved acid determined in the filtrate in the experimental data (II).

$$f(pH) = \frac{1}{(1+e^{(pK_{lw}-pH) \times Slope})} \times P \quad [1]$$

The sigmoid in was fitted to the experimental data by minimising the root mean squared error between the experimental data and the sigmoid equation. The pK_{lw} and slope factor were optimised alternately until the relative change in pK_{lw} and slope was below 0.01% for both parameters.

3.2.4 Colloidal stability of pitch in TMP suspensions (III)

TMP was soxhlet extracted with hexane, and with a mixture of acetone:water:acetic acid (90:9:1) to remove the lipophilic substances. Part of the TMP was peroxide bleached according to a laboratory procedure using diethylene triamine pentaacetic acid (DTPA), MgSO₄, H₂O₂ and NaOH. The extracted TMP, both unbleached (unbl.) and peroxide-bleached (p-bl.), was then washed repeatedly with 60°C distilled water.

Unbl. or p-bl. TMP was mixed with pitch emulsion. Different volumes of CaCl₂-solutions were added and the pH of the suspension was adjusted to 5 or 8 with NaOH at room temperature. The suspensions were stirred at 200 rpm by a magnetic stirrer for 1 h. After 1 h, the pH of the suspensions was

measured and the suspensions were then centrifuged at about 210 g for 15 min, to remove unstable aggregates of pitch, fines and fibres, and the supernatant was collected. Colloidal stability was in these experiments defined as the colloidal wood pitch that could withstand a centrifugation at 210 g for 15 min, and thus remained in the supernatant of the sample. The determined concentration of pitch in the supernatant was compared to the concentration in samples without added CaCl_2 , which were subjected to the same procedure.

3.2.5 Aggregation of DCS water with cationic polymers

TMP was diluted to 1% consistency with distilled water and the suspension was agitated at 150 rpm and 60°C for 4 h. The suspension was then centrifuged at 500 g for 30 min to remove fibres and fines. The supernatant, i.e. the DCS water, was pipetted off and used as such. The DCS water contained dissolved substances, mainly O-acetyl-galactoglucomannans and other hemicelluloses and pectins, and colloidal pitch droplets (Holmbom, Sundberg 2003). The concentration of wood pitch in the TMP water was about 50 mg/L. The pH of the DCS water was adjusted to 3, 5 or 8 with H_2SO_4 or NaOH. PolyDADMAC (Sigma-Aldrich, USA) with a molar mass of 100-200 kDa, and a charge density of about +6 meq/g was added to the DCS water to concentrations between 0 and 16 ppm (mg/L) and the mixture was stirred for 15 min. Experiments were also performed with cationic polyacrylamide (C-PAM, Percol 175, Ciba Specialty Chemicals, Raisio) with a molar mass of about 5000 kDa and a charge density of about +900 $\mu\text{eq/g}$. The samples were afterwards allowed to sediment for 20 min until the formed aggregates settled to the bottom of the beaker. The turbidity of the supernatant was measured with a Novasina analite nephelometer (model number 156), and plotted against the concentration of polyDADMAC or C-PAM in the sample.

3.2.6 Interactions between pitch and mineral particles (IV)

25 mL TMP pitch emulsion was measured into a bottle. Different volumes of GGM stock solution were added to the pitch emulsion, and the mixture was diluted to 50 mL with filtered distilled water. The starting concentration of colloidal pitch in the experiments was 186 mg/L, with a standard deviation of about 4%. The mixture was agitated using a magnetic stirrer throughout the experiment. Small doses of mineral slurry, i.e. PCC, GCC, kaolin or bentonite in water, was added to the mixture, and allowed to react for about 5 min. A

small sample was then pipetted from the mixture for analysis by flow cytometry.

3.2.7 Froth flotation (V; VI)

The flotation cell used was a 20 L laboratory Voith cell, working according to the principle of froth flotation, also known as induced air flotation. The cell consisted of a mixer at the bottom of a tank (Fig 3.2). 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.

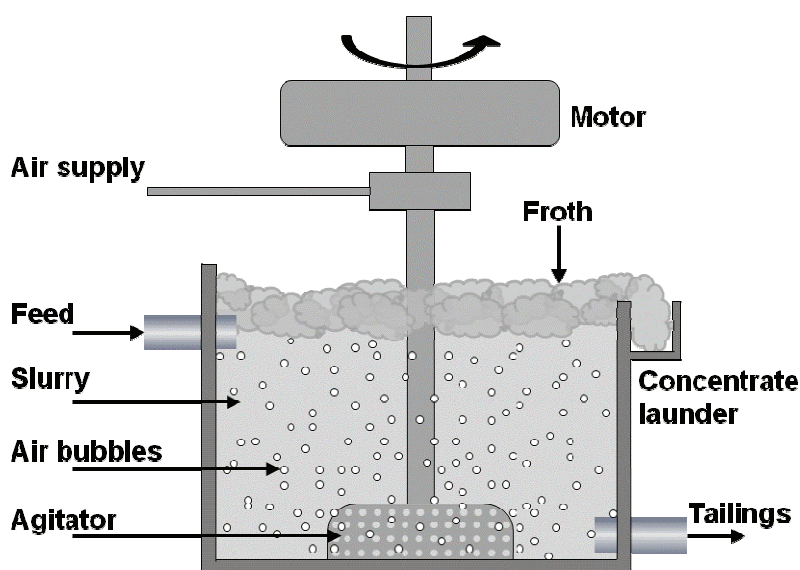


Figure 3.2 Schematic illustration of the laboratory froth flotation cell (V; VI).

Unbleached (V) or peroxide-bleached (VI) TMP water was obtained from a pulp mill using Norway spruce. The water was mixed vigorously before sampling, 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 dodecyltrimethylammonium chloride (DoTAC, China Innovation Group Co., Ltd, purity >99%) stock solution was

added to the beaker, and allowed to react for about 20 min under continuous mixing. 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. Samples of the TMP water were collected through the tailings tube after 60 min of flotation (Fig 3.2). The collapsed foam volume was measured in a graduated cylinder.

3.3 Analyses

3.3.1 Analysis of pitch components (I-VI)

The concentrations of pitch components in the samples were determined by gas chromatography using both long and short column techniques (Örså, Holmbom 1994; I-VI). The samples were acidified with H₂SO₄ to pH 3.5. 2 mL of internal standard, containing 0.02 mg/mL of heneicosanoic acid (21:0), betulinol, cholesteryl heptadecanoate (Ch17), and 1,3- dipalmitoyl-2-oleyl glycerol (triglyceride standard) in MTBE, was added to the sample. The MTBE phase was separated, dried and silylated. Analysis of steryl esters, diglycerides, and triglycerides was conducted on a short column with a PerkinElmer Clarus 500 gas chromatograph. The column was a HP-1, 7m x 0.53 mm and film thickness 0.15 mm. Hydrogen was used as carrier gas. The injection volume was 0.5 mL, on-column, and the detector used was a flame ionisation detector (FID).

Analysis of resin and fatty acids, lignans, and sterols was conducted on a long column with a PerkinElmer AutosystemXL gas chromatograph. The used column was a HP-1, 25 m x 0.2 mm, and film thickness 0.11 mm. Hydrogen was used as carrier gas. The injection volume was 1 mL, split 24:1, and the detector used was an FID.

3.3.2 Analysis of hemicelluloses and pectins (II-VI)

Analysis of the hemicelluloses and pectins was performed with acid methanolysis (Sundberg, A. et al. 1996; Willför et al. 2009). Pitch emulsion containing GGM, or GGM solution was freeze dried, and methanolysis reagent was added to the dry samples. The samples were then placed in an oven at 100°C for 3 hours. 1 mL of sorbitol or resorcinol solution (0.1 mg/mL in MeOH) was used as internal standard. The samples were silylated and left

over night at room temperature. The analysis of sugar units was conducted with a Varian 3400 gas chromatograph. The column used was a HP-1, 25m x 0.20 mm, and film thickness of 0.11 mm. Hydrogen was used as carrier gas. The injection volume was 1 mL, split about 20:1, and the detector used was an FID.

3.3.3 Flow cytometry (IV)

Flow cytometry (FCM) was performed with a Partec CyFlow Blue apparatus. The light scattered by the particles was recorded as forward scattering (FSC) and as side scattering (SSC, 90°). The cytometer was equipped with three different fluorescence channels; FL1 (512-542 nm, green), FL2 (575-605 nm, orange) and FL3 (615-645 nm, red). Filtered distilled water was used as sheath fluid in the analysis. The experimental samples were diluted 20-200 times with filtered distilled water prior to analysis, depending on the amount of particles in the sample. A methanol solution of Nile red (Tamro, Vantaa, Finland) was used to stain the lipophilic substances (Vähäsalo et al. 2003; Vähäsalo, Holmbom 2005). The red fluorescence intensity (FL3) was used as an indicator of the amount of lipophilic material on particle surfaces. The populations were gated using Partec FloMax software (v. 2.4f), which made it possible to calculate the mean hydrophobicity of the different particle populations (Vähäsalo et al. 2003).

3.3.4 Determination of charge on TMP fibres and mineral particles (III; IV)

The charge of unbleached (unbl.) TMP, peroxide-bleached (p-bl.) TMP (III), and all of the mineral particles used (IV), was determined by polyelectrolyte titration with 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide (polybrene, $\sim 8 \times 10^3$ Da, Sigma) and potassium polyvinyl sulphate (KPVS) through back-titration using a particle charge detector (Mütek PCD 03), also known as a streaming current detector (Holmbom et al. 2000). Suspensions were prepared with de-ionized water, and different doses of polybrene or KPVS were added to the suspensions during stirring. After 1 h the suspensions were filtered through glass fibre filters (VWR International, Glass microfiber, 691) (III), or syringe filters with a pore size of 0.2 (Titan 3, nylon membrane, Purple) or 0.1 μm (Whatman International Ltd., inorganic membrane filter, Anotop 25 Plus) (IV), depending on the size of the particles. The filtrates of the suspensions, as well as reference samples, were titrated

with KPVS or polybrene in the particle charge detector to determine the concentration of unadsorbed polybrene or KPVS. The determined concentrations from the measurements were used to plot adsorption isotherms, from which the particle charge could be extrapolated.

4. RESULTS AND DISCUSSION

4.1 Phase distribution of resin and fatty acids

The impact of dissolved and colloidal substances on pulping and papermaking applications has been studied previously (see e.g. Tanase-Opedal et al. 2011a). However, the importance of pH has not been fully acknowledged in these studies. Wood pitch is composed of several different components, some of which are insoluble in water, while others may be partly or completely water-soluble (Sjöström 1981). The aim of this chapter is to outline the water-solubility of pitch components as a function of pH, as well as a few other variables.

4.1.1 In a pitch emulsion

At pH 3, and below, all of the resin and fatty acids were associated with the colloidal pitch droplets, that is, were in the lipophilic phase (Fig 4.1). No resin or fatty acids were dissolved in the water phase. When pH was increased, the resin and fatty acids were gradually dissociated and also detached from the colloidal droplets and as a consequence dissolved in the water phase (I). At pH about 6, 50% of the resin acids were found in the lipophilic phase and 50% were dissolved in the water phase. This pH is here termed pK_{lw} (lipophilic phase-water phase). The fatty acids generally required a higher pH to be dissolved in the water phase than the resin acids. The average pK_{lw} for fatty acids was close to 9, and even at pH 10 only about 70% of the fatty acids were dissolved (Fig 4.1). The release of resin acids at lower pH than fatty acids was accredited to the bulky hydrocarbon skeletons of the resin acids (I). The process waters at mills using neutral papermaking can therefore contain very high concentration of dissolved resin acids. Hence, dissolved resin acids are recycled with the process water to a higher degree while the fatty acids are retained in the paper with the colloidal pitch droplets.

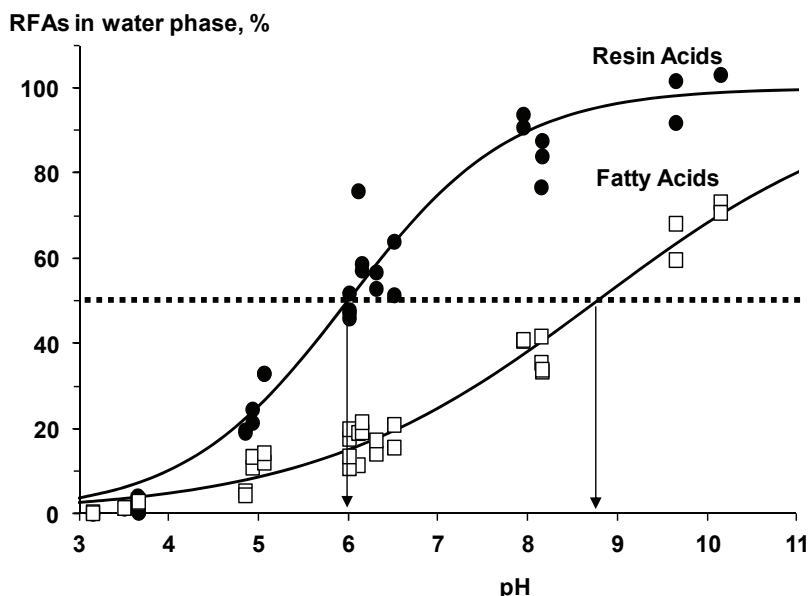


Figure 4.1 Distribution of resin and fatty acids (RFAs) between the colloidal, lipophilic phase and the water phase at 50°C and low NaCl concentration (I). The arrows show the “ pK_{lw} ” for resin acids (about 6) and fatty acids (close to 9). The concentrations were determined with long column GC and no additional fatty acids were added to the model pitch emulsion. The concentration of resin and fatty acids in the pitch emulsion was about 31 mg/L and 6 mg/L, respectively.

To determine the pK_{lw} -values for the individual fatty acids, saturated fatty acids were added to the wood pitch before preparing the emulsion in order to increase the concentration of these. The fatty acids required a quite high pH to become dissolved in the water phase and large differences were found between the phase distributions of individual fatty acids (Fig 4.2). The pK_{lw} -values depended strongly on both the chain length and the number of double bonds in the chain. The pK_{lw} for palmitic acid (16:0) was about 7.4, for stearic acid (18:0) about 10.1, and between 12.5 and 13.1 for arachidic acid (20:0), behenic acid (22:0) and lignoceric acid (24:0). The effect of chain length levelled out after arachidic acid (20:0).

Introduction of double bonds into the hydrocarbon chain of the fatty acid decreased its pK_{lw} -value, for example, the pK_{lw} -values of oleic (18:1) and linoleic acid (18:2) were significantly lower than for stearic acid (Fig 4.2).

Introduction of one double bond into the hydrocarbon chain lowers the hydrophobicity equally to the removal of one methylene group from the fatty acid chain (Ström 2000). This was also seen in these measurements, since the phase distribution and pK_{lw} of palmitic acid (16:0) and linoleic acid (18:2) were quite similar (Fig 4.2). Introduction of a double bond causes a bend in the structure of the fatty acid chain; the fatty acid chain requires a larger space to rotate, which will lower the intermolecular association of the carbon chains (Ekman, Holmbom 2000; Kanicky, Shah 2002). This means that unsaturated fatty acid chains cannot be packed as closely as the chains of saturated fatty acids (Fig 2.3). The measurable colloidal pK_a -values of fatty acids also decrease when double bonds are introduced into the hydrocarbon chain (Kanicky, Shah 2002).

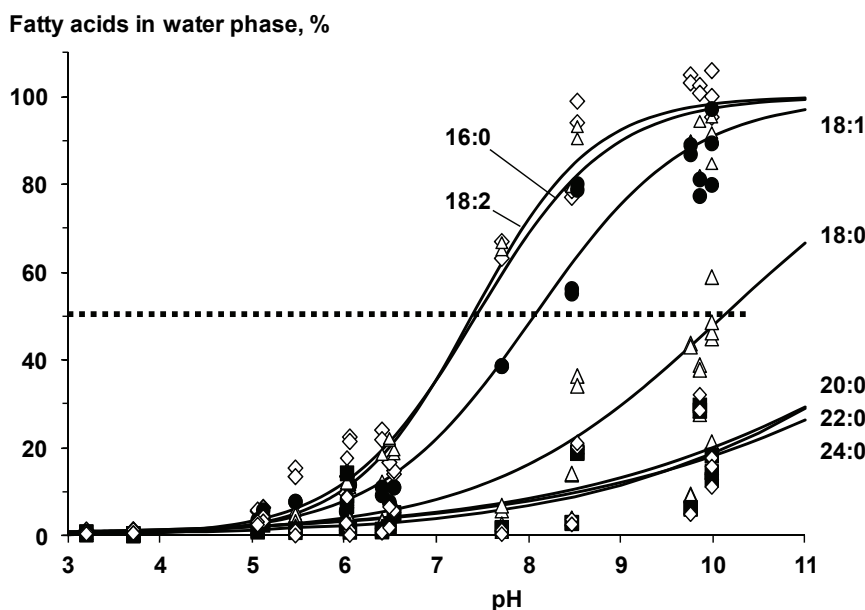


Figure 4.2 Distribution of some fatty acids between the lipophilic phase and the water phase at 50°C in a wood pitch emulsion with added saturated fatty acids (I). The concentration of resin and fatty acids in the pitch emulsion was about 32 mg/L and 21 mg/L, respectively.

The individual resin acids also showed some differences in their pH-dependent phase distribution (Fig 4.3). The pK_{lw} -value was significantly lower for dehydroabietic acid, about 5.3, than for the other resin acids, having values between 6.7 and 7.2. The essential difference in the structure of these

resin acids is the aromatic ring in dehydroabietic acid (Fig 2.1) that is a strong electron-withdrawing group, which increases the water-solubility (Nyrén, Back 1958). No significant difference was seen in the pK_{lw} -values between the other abietic type of resin acids and the pimaric type (Fig 4.3).

The pK_{lw} -value of dehydroabietic acid in a pitch emulsion without added salt was 5.3, which is considerably lower than the previously published colloidal pK_a -value of dehydroabietic acid, i.e. 6.18 (McLean et al. 2005a). This indicated that the water-solubility of resin acids in wood pitch emulsions with insoluble, hydrophobic substances, are not solely determined by the colloidal pK_a -values.

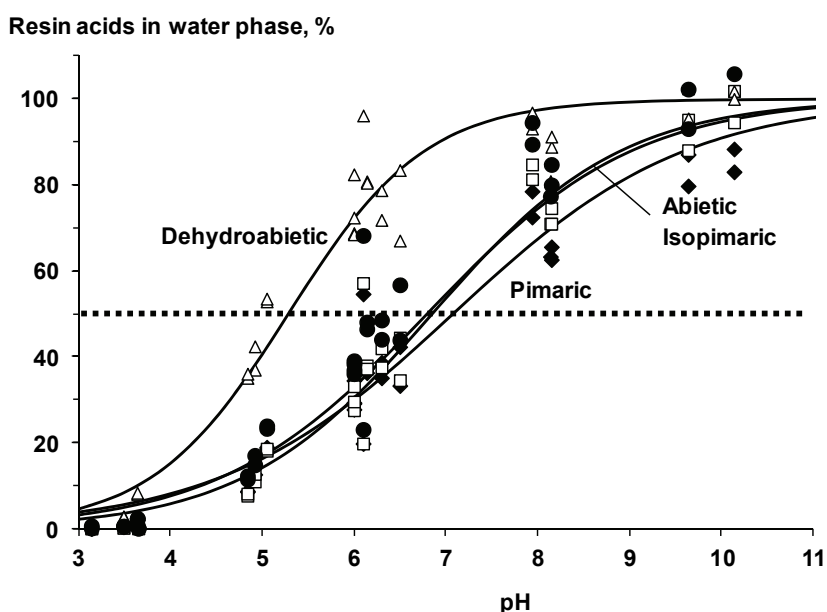


Figure 4.3 Distribution of some resin acids between the lipophilic phase and the water phase at 50°C in a wood pitch emulsion without added saturated fatty acids (I). The concentration of resin and fatty acids in the pitch emulsion was about 31 mg/L and 6 mg/L, respectively.

4.1.2 In the presence of sodium chloride

The concentration of metal ions in process waters varies constantly due to factors such as differences in raw material feedstock, the amount of deinked pulp used, the hardness of the raw water, the type of fillers used, etc. (Neimo

1999; Stenius 2000; Werkelin et al. 2005; Granholm 2011). It is known that an increased salt concentration influences the colloidal pitch by compression of the electric double layer surrounding the pitch droplets (Eklund, Lindström 1991). At a certain concentration, the droplets will be aggregated and no longer colloidal; this concentration depends strongly on the valency of the metal ion (Sundberg, K. et al. 1994a; Lee 2011). It was therefore of interest to also determine if an increased salt concentration has any influence on the phase distribution of RFAs.

Higher NaCl concentrations resulted in a release of RFAs at a higher pH compared to conditions without NaCl, as illustrated by the phase distribution of abietic acid (Fig 4.4). Most of the pK_{lw} -values for the individual resin and fatty acids increased with increasing NaCl concentrations (I). The largest difference was seen between low salt concentration and 10 mM NaCl. It is known that addition of Na^+ ions leads to decreased repulsion between ionic end groups of sodium oleate, which increases its tendency to form micelles (Ödberg et al. 1985). The pK_{lw} of the RFAs also increased in the presence of NaCl, possibly due to lowered repulsion by the ionic carboxyl groups in the surface layer of the pitch droplets. It has previously been suggested that cooperativity between fatty acid chains and head groups may increase the measured pK_a of fatty acids in films (Kanicky et al. 2000). Adjusting the pH to alkaline conditions with NaOH also increased the concentration of Na^+ in the emulsion slightly. This concentration was, however, much lower than 10 mM NaCl.

Sodium soaps of RFAs are quite soluble in water (Palonen et al. 1982), and additions of NaCl only resulted in a shift in pK_{lw} towards higher pH (I). Phase distribution experiments with $CaCl_2$ have shown that the type of metal ions play an important role in understanding the pK_{lw} of RFAs (MacNeil et al. 2011). Calcium soaps of fatty acids have a very low solubility in water even at pH 11, which means that the pK_{lw} of fatty acids is shifted towards extremely high pH in the presence of low concentrations of calcium ions. The maximum solubility of most resin acids is also diminished by addition of $CaCl_2$, while not as much as for the fatty acids. E.g. the solubility of abietic acid at pH 11 was about 100% with 0 mM $CaCl_2$, while it was only 45% with 10 mM $CaCl_2$. It is reported that the water-solubility of Ca-oleate and Ca-abietate is very low at concentrations below their critical micelle concentration (Palonen et al. 1982).

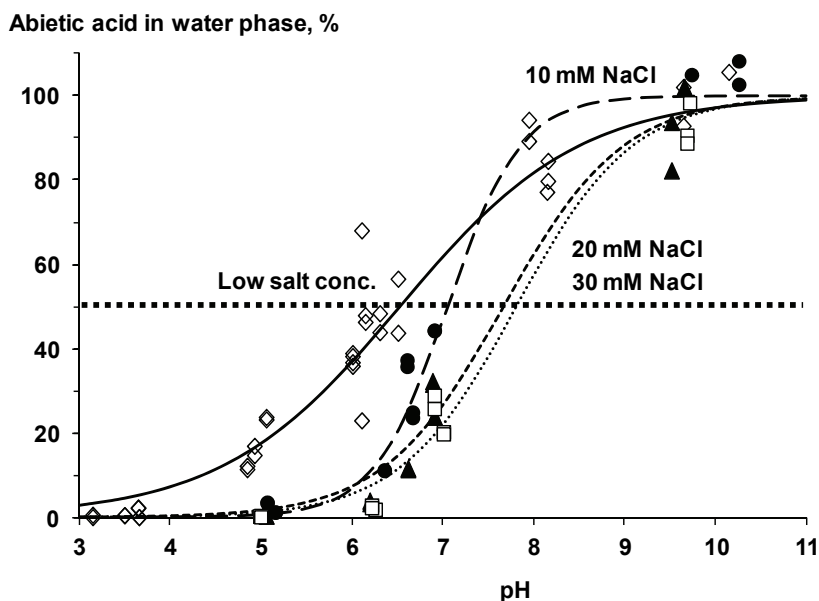


Figure 4.4 Distribution of abietic acid between the lipophilic phase and the water phase at different NaCl concentrations in a wood pitch emulsion (I). The temperature was 50°C. The concentration of resin and fatty acids in the pitch emulsion was about 31 mg/L and 6 mg/L, respectively.

4.1.3 With varying pitch composition

The pitch composition in process waters experience seasonal variations; the concentration of triglycerides is generally lower in summer months due to hydrolysis of triglycerides into fatty acids. Seasoning of the wood, as well as enzymatic treatment of the wood raw material, causes variations in the feedstock entering the pulping and papermaking process (Ekman 2000; Rundlöf et al. 2002).

Pitch emulsions with high ratio of triglycerides to RFAs (High) was composed of triglycerides (TG):resin acids (RA):fatty acids (FA) at a ratio of 5.1:1.5:1.0. Pitch emulsions with significantly lower ratio of triglycerides to RFAs (Low) was composed of TG:RA:FA at a ratio of 2.0:1.5:1.0 and used to simulate pitch in process water after effective seasoning or enzymatic treatment (II). The results showed that the TG to RFA ratio had a significant effect on the phase distribution of RFAs at different pH (Fig 4.5). The average

pK_{lw} of the resin acids was 1.4 pH units lower in the emulsions with low TG to RFA ratio compared to in the emulsions with high TG to RFA ratio. The decrease in pK_{lw} for the individual resin acids was 1.2-1.8 pH units (II), and the largest decrease was seen for dehydroabietic acid, i.e. the least hydrophobic resin acid. About 85% of the resin acids were found in the water phase at pH 7.5 in emulsions with both high and low TG to RFA ratio, and the maximum solubility was also quite similar in the two different emulsions (Fig 4.5). The results show that the phase distribution of resin acids was significantly influenced by the TG to RFA ratio only at pH below 8. Similar trends were also seen for the fatty acids, while the differences were not as large as for the resin acids. It was recently proposed that at low TG:RFA ratios the resin acids may be present as a cloud surrounding the colloidal pitch droplets, while the fatty acids are actually attached to the lipophilic pitch colloids (Lee 2011; see 2.3). This type of bi-layered structure could have enabled the loosely associated resin acids to pass the syringe filter at pH 5 (Fig 4.5). A shift in the pK_{lw} of RFAs was also observed when comparing the results from phase distribution experiments with added saturated fatty acids to experiments without added fatty acids (I), i.e. changes in the pitch composition altered the pK_{lw} .

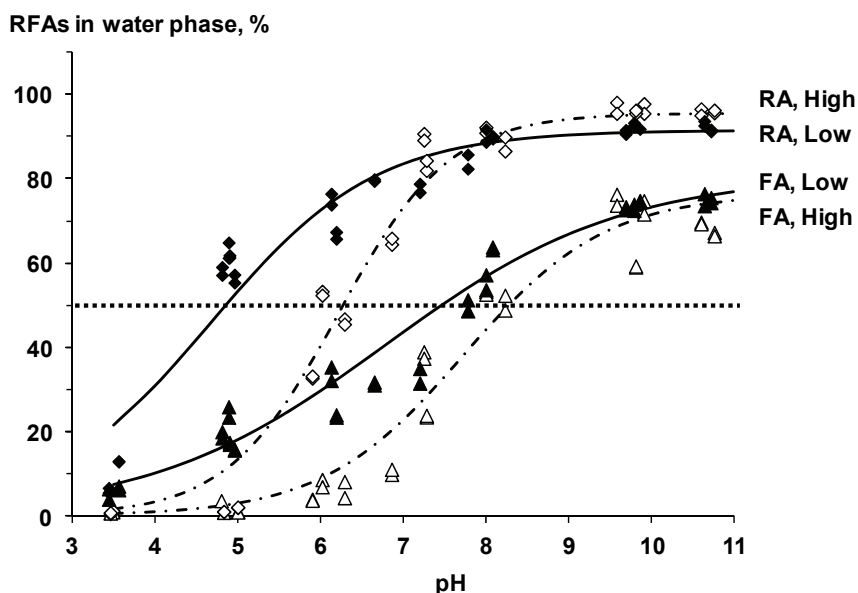


Figure 4.5 Distribution of resin acids (RA) and fatty acids (FA) between the lipophilic phase and the water phase in pitch emulsions with a high ratio of triglycerides to RFAs (High, dotted line), and low ratio of triglycerides to RFAs (Low, solid line) at 50°C. The RA concentration was 26 mg/L and the FA concentration was 17 mg/L in the high-emulsion. The RA concentration was 19 mg/L and the FA concentration was 13 mg/L in the low-emulsion.

4.1.4 Kinetics at rapid pH changes

The pH in papermaking is ever changing; mechanical pulping is done at acidic pH, peroxide bleaching is performed at alkaline pH, and the papermaking process is nowadays mostly done at neutral or slightly alkaline pH. Water streams with different pH-values may be combined, resulting in sudden variations in local pH. It was therefore of interest to determine the kinetics of the dissolution/adsorption of RFAs between the lipophilic phase and the water phase.

The pH was adjusted to 5 and was then rapidly increased to 8, after which samples were taken and immediately filtered. Already at the first measurement point, i.e. after 0.5 min, practically all of the resin acids and 35% of the fatty acids were dissolved (Fig 4.6). The results were compared to the phase distribution curves at equilibrium after 3 h (Fig 4.1). It was evident that

the dissolution of RFAs from the lipophilic phase to the water phase takes place very quickly after a rapid pH increase. It was also seen that the adsorption of RFAs takes place very quickly after a rapid decrease in pH (I).

Changes in pH will immediately change the concentration of dissolved RFAs, which will affect pitch control during papermaking. Combining two water streams with different pH may cause a sufficiently large pH shock for pitch problems to occur, especially in the presence of a high concentration of calcium ions (MacNeil et al. 2011).

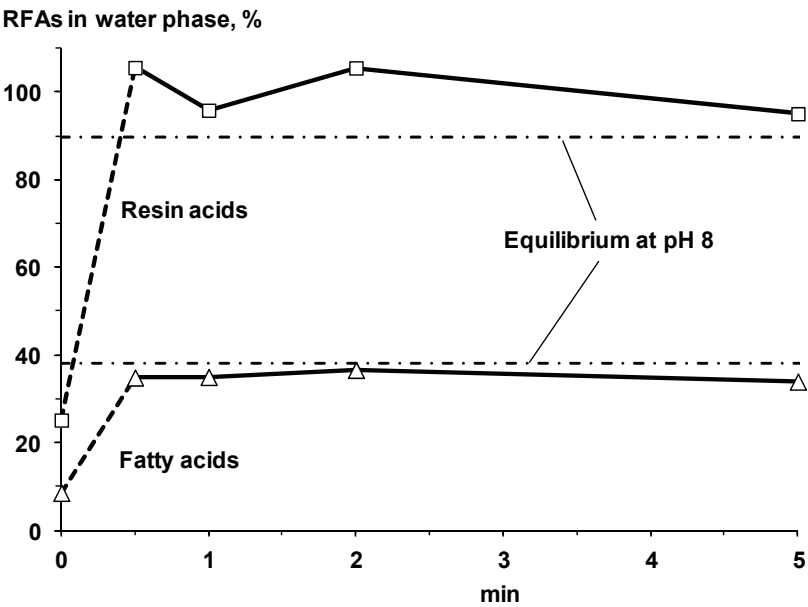


Figure 4.6 Distribution of RFAs between the lipophilic phase and the water phase after sudden pH change from 5 to 8 at 50°C. The dotted lines represent the equilibrium after 3 h at pH 8 (I).

4.1.5 Summary

Resin and fatty acids are present in pitch emulsions in either colloidal or dissolved form depending primarily on pH (Fig 4.7). The pH-value at which 50% of an individual resin or fatty acid is associated with the lipophilic pitch droplets (l), and 50% is found in the water phase (w), is termed pK_{lw} , i.e. the phase distribution constant. The pK_{lw} -values of fatty acids depend on their chain length and the amount of double bonds in the chain. The resin acids are released from the lipophilic pitch droplets at lower pH than fatty acids due to their bulky structure, which reduces their packing possibilities in a surface layer. The release of RFAs from the pitch droplets to the water phase shifts towards higher pH in the presence of salts. The phase distribution of RFAs, and subsequently their pK_{lw} , is also influenced by pitch composition; a lower triglyceride ratio in the pitch results in lower pK_{lw} -values. The dissolution or adsorption of RFAs at a sudden pH-change takes place very quickly.

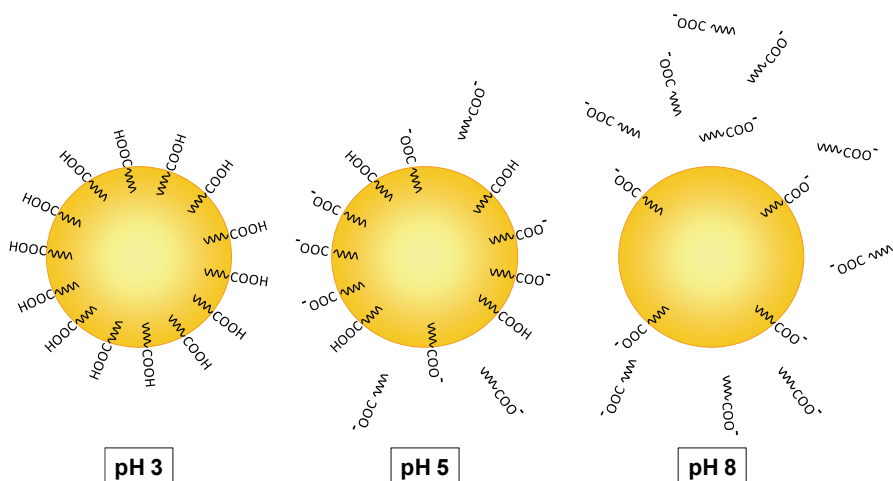


Figure 4.7 Schematic illustration of colloidal wood pitch at different pH levels. The phase distribution of resin and fatty acids is shifted from the lipophilic pitch droplets (l) to the water phase (w) with increasing pH.

4.2 Destabilisation of colloidal pitch

Uncontrolled aggregation of colloidal wood pitch usually leads to pitch problems and deposits (see e.g. Tanase-Opedal et al. 2011a). Colloidal pitch is mixed with fibres, fines, mineral particles, as well as dissolved and colloidal substances in the process waters of a paper machine. In the presence of fibres or other particles, pitch-pitch collisions are no longer the only possible mechanism causing aggregation and destabilisation. The aim of this chapter is to determine how the colloidal stability of pitch is influenced by the presence of fibres and mineral particles.

4.2.1 By mechanical fibres

Resin and fatty acids (RFAs) are found both in dissolved and colloidal form depending on pH (I; II). The neutral pitch components, i.e. steryl esters and triglycerides, are only found in colloidal form due to their low solubility in water (Sjöström 1981; Back 2000). Information about the colloidal stability of pitch can therefore best be derived from the concentrations of neutral pitch components in the supernatant of the samples. The colloidal pitch was only stabilised electrostatically, since the experiments were conducted in the absence of water-soluble hemicelluloses, which give steric stabilisation to the colloids.

With no TMP present, the colloidal stability of the pitch was impaired by additions of CaCl_2 at both pH 5 and 8 (Fig 4.8). The pitch was more stable towards electrolyte-induced aggregation at pH 8 than at pH 5. This stability-increase was most likely caused by dissociation of carboxyl groups of RFAs, which resulted in higher anionic charge of the pitch at pH 8 (Sundberg, K. et al. 1996b). The mechanisms behind electrolyte-induced destabilisation of pitch have been described as compression of the electrical double layer of the pitch droplets, possibly combined with direct chemical reactions between soap anions and metal cations (Sundberg, K. et al. 1994a; Back 2000; Hannuksela, Holmbom 2004; Stack et al. 2011). When no TMP is present, the destabilisation of pitch is most probably caused by pitch-pitch collisions, since no other available surfaces are present (Allen 1980).

In absence of CaCl_2 , no destabilisation of colloidal pitch occurred in the presence of 1% unbleached (unbl.) or peroxide-bleached (p-bl.) TMP, i.e. the repulsion between the fibres and the colloids was sufficient to prevent

collisions leading to aggregation (Fig 4.8; III). The repulsion between fibres and colloids was significantly diminished by additions of CaCl_2 , due to compression of the electrical double layers surrounding both fibres and colloids (Hassler 1988; Back 2000). It has also been reported that colloidal wood pitch has no affinity to bleached kraft pulp in the absence of NaCl, and that no deposition onto polypropylene surfaces in absence of electrolytes occurs (Sundberg, K., Holmbom 1997; Qin et al. 2004).

The pitch was more stable against 1 mM CaCl_2 in suspensions of p-bl. TMP than in suspensions of unbl. TMP. The repulsion between p-bl. TMP fibres and colloidal pitch was stronger than the repulsion between unbl. TMP and pitch because of the difference in fibre charge. The determined anionic charge of the p-bl. TMP was 199 $\mu\text{eq/g}$, while the anionic charge of unbl. TMP was only 84 $\mu\text{eq/g}$, which was in agreement with previously published results (Fardim et al. 2002). The added calcium ions probably adsorbed primarily to the TMP fibres, since the pK_a -values of the charged groups on fibres are lower than the pK_a of RFAs, 3.5-4.0 and 5.5-6.4, respectively (Holmbom et al. 2000). Therefore, a higher concentration of calcium ions was needed in order to neutralise the charge of the p-bl. fibres before fibre-colloid interactions occurred. It has been reported that about 10 mM CaCl_2 or 200 mM NaCl is needed to completely destabilise a wood pitch emulsion without hemicelluloses (Sundberg, K. et al. 1994a).

At pH 5, the concentration of RFAs in the supernatant decreased in the same rate as the neutral pitch, with and without TMP (III). At pH 8, the fatty acids still followed the same pattern as the neutral pitch, but about 40% of the resin acids remained in the supernatant even at 10 mM CaCl_2 (III) as water-soluble calcium soaps (Allen 1988; MacNeil et al. 2011). It has been reported that deposits, by deposition tests onto steel foils, contain less resin acids at pH 8 than at pH 5 in the presence of calcium (Saarimaa et al. 2006c). The deposition behaviour of colloidal pitch has been linked to the solubility of the different groups of pitch components at varying pH; especially the solubility of resin acids in papermaking processes using *Pinus radiata* (McLean et al. 2005b).

Neutral pitch components in supernatant, %

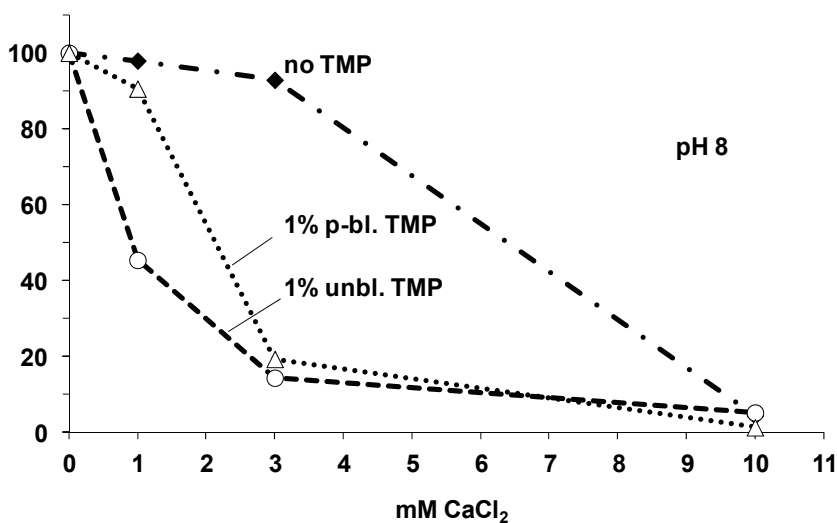
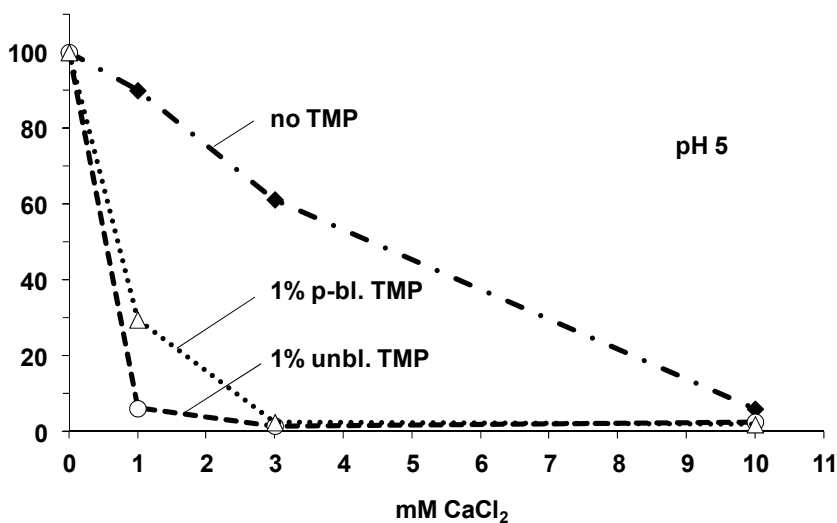


Figure 4.8 The concentration of neutral pitch components in the supernatant after CaCl₂-additions to suspensions of no TMP, 1% peroxide-bleached (p-bl.) TMP and 1% unbleached (unbl.) TMP, at pH 5 and 8 (III).

4.2.2 By mechanical fibres and added GGM

It is known that water-soluble galactoglucomannans (GGM) stabilise pitch sterically against electrolyte-induced aggregation (see e.g. Hannuksela, Holmbom 2004). Most studies showing this have been performed in the absence of solid particles or fibres, or using DCS from peroxide-bleached and unbleached TMP (Sundberg, K. et al. 1996a). It was therefore of interest to quantitatively determine the steric stabilisation of colloidal pitch by GGM using the same pitch emulsion in different well-defined suspensions of TMP.

Addition of 90 mg/L of GGM to the colloidal pitch emulsions completely stabilised the pitch towards aggregation by CaCl_2 at pH 5 in the absence of TMP fibres (Fig 4.9). It has previously been shown that 100 mg/L of native O-acetyl-GGM can completely stabilise a colloidal pitch emulsion against even 30 mM of CaCl_2 at low pH (Hannuksela, Holmbom 2004), while only 10 mM CaCl_2 is needed to destabilise a pitch emulsion without GGM (Sundberg, K. et al. 1994a). The stabilising mechanism was described as steric stabilisation (Welkener et al. 1993; Sundberg, K. et al. 1994a; 1996a; Puro et al. 2011).

Addition of p-bl. TMP to the pitch emulsion and GGM, in combination with CaCl_2 , diminished the colloidal stability of the pitch (Fig 4.9). The repulsion between fibres and colloids was significantly diminished due to compression of their electrical double layers, as was the case in the experiments without GGM (Fig 4.8). The colloidal stability of the pitch in suspensions of TMP was, however, much higher with added GGM, and even the highest concentration of CaCl_2 was not enough to completely destabilise the pitch (Fig 4.9). The stability of the pitch was further diminished when the TMP-consistency was increased from 0.25 to 0.5 and 1%. Similar trends were also seen at pH 8 (III). A higher TMP-consistency results in more pitch-fibre collisions, which can lead to aggregation and destabilisation of the colloidal pitch (Hassler 1988; Wågberg, Ödberg, 1991; Back 2000). It is known that steric stabilisation by GGM reduces the deposition tendencies of pitch (Otero et al. 2000). These results show that the interactions between colloidal pitch and solid surfaces cannot be completely avoided by addition of GGM, in the presence of CaCl_2 .

The concentration of GGM in the supernatant was not significantly affected by the changes in pitch composition throughout the experiments, neither at pH 5 nor at pH 8 (III). This indicated that the water-soluble GGM had no

mentionable tendency to be attached to TMP or pitch surfaces, which is agreement with previous studies (Hannuksela et al. 2003; Qin et al. 2004).

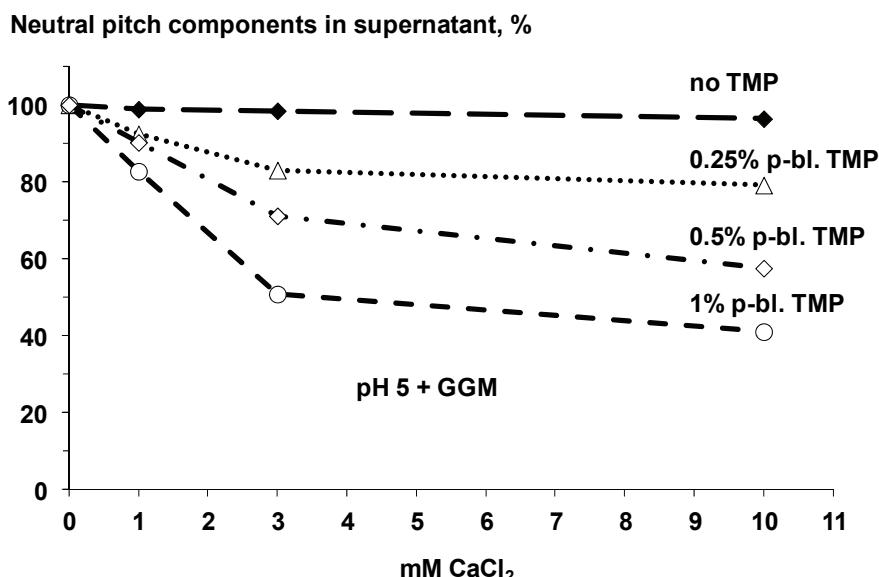


Figure 4.9 The concentration of neutral pitch components in the supernatant after CaCl₂-additions to suspensions containing GGM and no TMP, 0.25, 0.5, and 1% peroxide-bleached (p-bl.) TMP at pH 5 (III).

4.2.3 By cationic polymers

Cationic polymers are often used in papermaking to control dissolved and colloidal substances, which would otherwise accumulate in the process water and cause problems with runnability (Wågberg, Åsell 1995). The effectiveness of polymers for flocculating DCS has been previously investigated by the use of different polymers with different molar masses and charge densities (e.g. Sundberg, A. et al. 1994; Nurmi et al. 2004; 2006). The pH has a very significant influence on the phase distribution of pitch components (I; II), as well as the colloidal stability of pitch (III). It was therefore of interest to also determine whether pH has any significant effect on the aggregation of colloidal pitch in DCS water from Norway spruce TMP by cationic polymers.

PolyDADMAC is a polymer with low molar mass and a high charge density, which acts according to the patch flocculation mechanism, and flocculation

only occurs during a narrow concentration interval around the point of charge reversal (Eklund, Lindström 1991). At pH 5, three distinct stages were clearly observed when adding polymer to the DCS water, which was in agreement with previously published results (Wågberg, Ödberg 1991; Nylund et al. 1995). A polyDADMAC concentration of 0-6 ppm caused only a slight decrease in turbidity (Fig 4.10), i.e. the polymer concentration was too low to cause any significant aggregation of colloidal pitch. A large decrease in turbidity was observed with additions of 7-9 ppm polyDADMAC, which showed that aggregation/destabilisation occurred. It has been shown that pitch colloids form aggregates that are susceptible to sedimentation around the point of charge reversal (Wågberg, Ödberg 1991; Nylund et al. 1995). PolyDADMAC concentrations above 9 ppm resulted in similar turbidity values as with 0-6 ppm polyDADMAC; the colloidal pitch was then stabilised by an excess of cationic charges from the polyDADMAC (Nurmi, Eklund 2000). Some of the added polyDADMAC might also have formed complexes with the dissolved hemicelluloses present, but these complexes would not necessarily cause any significant changes in turbidity (Nylund et al. 1995).

The experiments were also performed at pH 3 and at pH 8. The polyDADMAC concentration needed to aggregate the DCS was significantly lower at pH 3 than at pH 5, while the concentration needed at pH 8 was significantly higher (Fig 4.10). This was in agreement with previously published results, which showed that the flocculation intensity of DCS decreased with increasing pH (Nurmi et al. 2004). Increasing the pH has also been shown to shift the optimal aggregation concentration towards higher values in experiments with Pine xylan and cationic polymers (Ström et al. 1985). This was accredited to increasing anionic charge of the xylan, as well as lowered charge density of the used polyethyleneimine at higher pH. However, it has been reported that the charge of polyDADMAC is largely independent of pH (Nicke et al. 1992; Wu et al. 2010). The polyDADMAC concentration needed for aggregation of the DCS ranged between 3 and 13 ppm, depending only on pH in these experiments. The optimal polyDADMAC concentration was shifted towards higher values with increasing pH mainly due to the increasing anionic charge of the DCS.

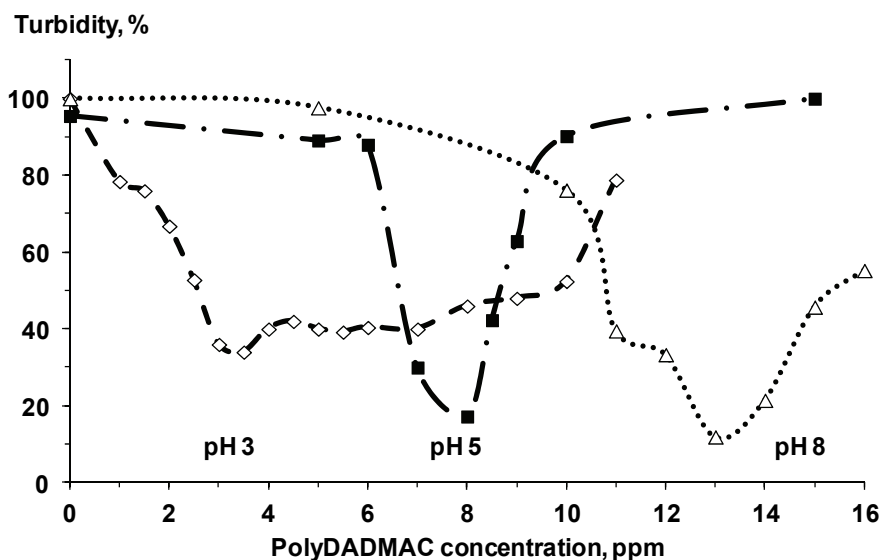


Figure 4.10 The turbidity of DCS water from Norway spruce TMP plotted against polyDADMAC concentration at pH 3, 5 and 8.

Experiments were also performed by adding cationic polyacrylamide (C-PAM) to DCS water. C-PAM is a polymer with much higher molar mass than polyDADMAC; 5000 kDa compared to 100-200 kDa. The C-PAM concentration for optimal flocculation was lowest at pH 3 and shifted towards higher concentrations with increasing pH (Fig 4.11) in a similar fashion to the experiments with polyDADMAC. It has previously been shown that the anionic charge of DCS increases with increasing pH (Sundberg, K. et al. 1996b). It has also been shown that colloidal pitch was more stable against electrolyte-induced aggregation by calcium ions at pH 8 compared to at pH 5 (Fig 4.8; III), which was attributed to increasing anionic charge of colloidal pitch with increasing pH. However, it has been reported that the charge density of C-PAM can decrease with increasing pH (Maher et al. 2007). This indicates that the high polymer concentration required for aggregation of pitch at pH 8 was a co-effect of the increased anionic charge of the pitch and the lowered cationic charge density of the C-PAM.

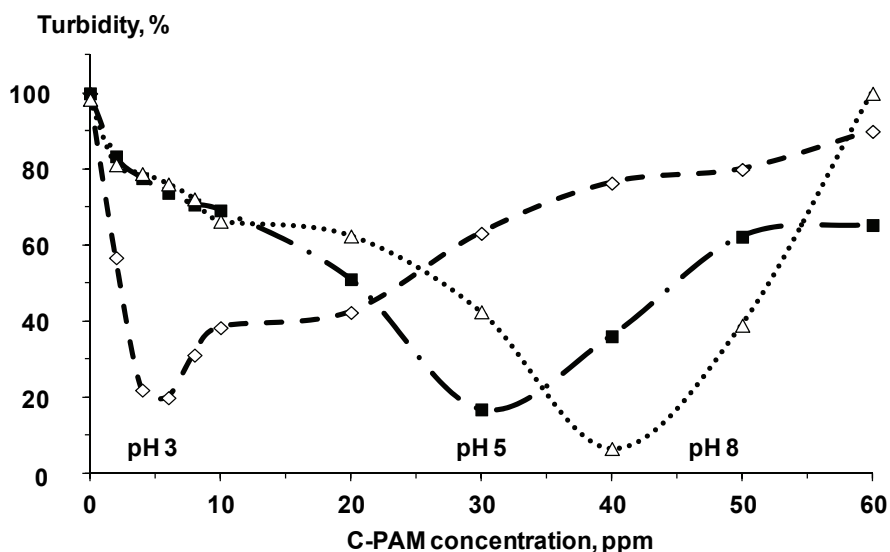


Figure 4.11 The turbidity of DCS water from Norway spruce TMP plotted against C-PAM concentration at pH 3, 5 and 8.

4.2.4 By mineral particles

Mineral particles, such as kaolin, bentonite, talc, ground calcium carbonate (GCC), and precipitated calcium carbonate (PCC), are nowadays widely used in papermaking applications. These minerals are found in the process waters alongside dissolved and colloidal substances from wood, and are also found as inorganic constituents in deposits (Sithol  2000). The interactions between wood pitch and mineral particles were of interest in order to get an insight into the mechanisms leading to deposition, and how deposits may be avoided in papermaking.

Samples of colloidal wood pitch, kaolin, GCC, PCC or bentonite were analysed separately by flow cytometry (FCM). The light scattering in forward direction (FSC) of the particles was plotted against the intensity of fluorescence in the 615-645 nm range (FL3) of the particles (Fig 4.12). FSC is an indirect measurement of particle size, which is also influenced by the refractive index of the particles. The intensity of light in the FL3 region is a measurement of the hydrophobicity of the particle surface. Nile red was used to stain the lipophilic substances in the samples (IV).

The most hydrophobic pitch components in the colloidal wood pitch, i.e. triglycerides and sterol esters, are shielded from the surrounding water by a surface layer of resin and fatty acids, but the nature of a pitch droplet is still quite hydrophobic. The FL3 values for colloidal wood pitch stretched from about 0.5 to 100, with a mean value of about 9 (Fig 4.12a). Particles with FL3 > 2 can be considered as hydrophobic.

The FL3 mean values for kaolin and GCC particles was about 0.2 (Fig 4.12b,c), indicating that very little Nile red were adsorbed onto these mineral surfaces, and that the mineral particles were quite hydrophilic. It is known that charged mineral surfaces have a tendency to form hydrogen bonds with the surrounding water (Solomon, Hawthorne 1983b). Most aluminosilicate minerals have highly polar surfaces that are hydrophilic. The hydrophobicity of the kaolin particle population was lower in this study compared to previously published hydrophobicity of kaolin as seen by FCM (Leiviskä et al. 2012). The low hydrophobicity of the kaolin particles implied that the amount of adsorbed contaminants was much lower in this study.

PCC A and PCC B particles (Fig 4.12d,e) gave similar FL3 values as kaolin and GCC pigments. Most of the bentonite A and B particles had FL3 values below 0.1 (Fig 4.12f,g), and were thus extremely hydrophilic. The flow cytometer used was set up in such a way that the lower limit of detection of particles was around 0.1 μm and the lower limit for FL3 was 0.1. Particles that were smaller than 0.1 μm and that emitted less light in the FL3 region than 0.1 were therefore not visible in the measurements. Bentonite C, had FL3 values ranging from 0.1 to 10 (Fig 4.12h), which showed that some of the particles were much more hydrophobic than bentonite A and B. The bentonite samples showed that large variations are possible between similar products. The FCM analyses showed that all the tested mineral pigments were quite hydrophilic, except bentonite C, which also contained particles that could be considered hydrophobic.

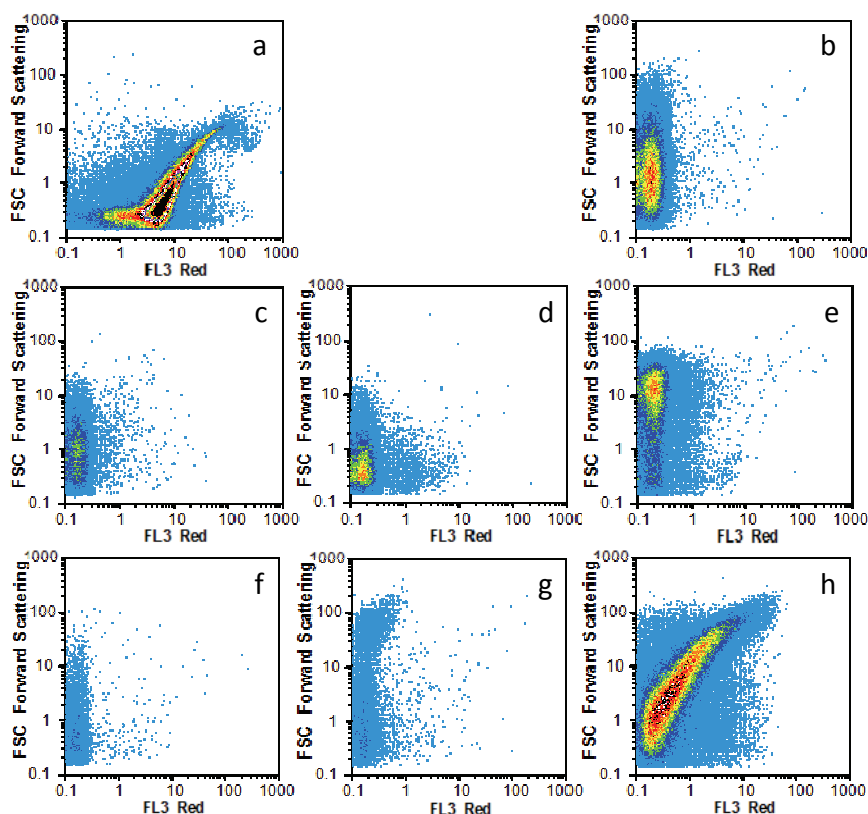


Figure 4.12 Logarithmic plots of the light scattering in forward direction (FSC) versus the intensity of fluorescence in the FL3 region (hydrophobicity) of various particles. Plot a) Colloidal wood pitch; b) Kaolin; c) GCC; d) PCC A (prismatic); e) PCC B (scalenohedral); f) Bentonite A; g) Bentonite B; h) Bentonite C (IV).

Additions of 530 ppm prismatic PCC (PCC A) to a pitch emulsion resulted in a new population seen by FCM, due to interactions between the pitch and the PCC (Fig 4.13). The newly formed population was slightly less hydrophobic than colloidal pitch, but more hydrophobic than PCC A as such (Fig 4.12a,d), which implied that the PCC A particles were not completely covered by pitch.

Increasing the PCC A concentration resulted in a more broad distribution of pitch-PCC A particles along the FL3-axis (Fig 4.13) (IV). The mean hydrophobicity of the pitch-PCC A population decreased when more PCC was added. This was due to the introduction of additional hydrophilic PCC

particles to the mixture, in combination with the lowered concentration of unadsorbed colloidal pitch. Deposition experiments with DCS on oxide surfaces have previously stated that pitch does not deposit onto surface layers of deposited DCS, i.e. a clean oxide surface is needed for adsorption of pitch (Kekkonen, Stenius 1999). This could be an explanation why the prismatic PCC only adsorbed a certain amount of pitch, and why the pitch did not continue to accumulate on top of the adsorbed pitch.

Additions of scalenohedral PCC (PCC B) to the pitch emulsion resulted in a population of pitch-PCC B particles with an even higher FL3 value than colloidal pitch (Fig 4.13). Increasing the concentration of PCC B from 530 to 2000 ppm further increased the hydrophobicity of the PCC B-pitch population, while depleting the original pitch population. Increasing the concentration of PCC B even further, to 3000 ppm, showed that more particles were formed in the FL3 range of 0.3-1, i.e. the particles were much less hydrophobic than the first pitch-PCC B population (Fig 4.13). The scalenohedral PCC added after 3000 ppm was not covered by pitch to the same degree, since the pitch population had been depleted prior to this.

PCC A and B both consist of calcium carbonate, but PCC A was anionic (-72 $\mu\text{eq/g}$ at pH 7), while PCC B was cationic (+39 $\mu\text{eq/g}$ at pH 9) (IV). Most collisions between PCC A and colloidal pitch did not lead to adsorption due to repulsion between the anionic charges, i.e. the formed pitch-PCC A population was less hydrophobic than the pitch by itself. The cationic PCC B was much more susceptible to pitch adsorption. Attraction between the anionic charges of the colloidal pitch and the cationic charges of PCC B lead to extensive interactions between these particles. The pitch most likely accumulated within the scalenohedral structure, and seemed to completely cover the surface of PCC B.

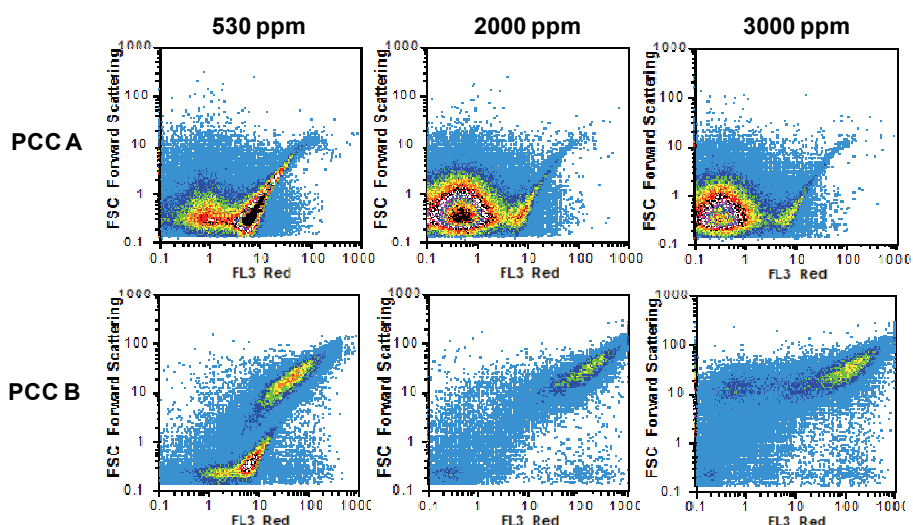


Figure 4.13 Light scattering versus hydrophobicity of colloidal pitch droplets with prismatic PCC (PCC A), and scalenohedral PCC particles (PCC B) plotted in logarithmic scale (IV).

The interaction between colloidal wood pitch and mineral particles is a quite complex system, since the pitch droplets consist of a mixture of resin acids, fatty acids, steryl esters and triglycerides. Rogan (1994) showed that montmorillonite adsorbed oleic acid quite effectively, while much less triolein was adsorbed. Miyanishi et al. (2000) showed that PCC adsorbed both oleic and abietic acid, and also that about ten times more oleic acid was adsorbed than abietic acid. The cationic charge of the PCC particles were most likely neutralised by the anionic fatty or resin acids, which caused aggregation of PCC particles. The large difference in hydrophobicity between the pitch populations formed with anionic PCC A particles and cationic PCC B showed that the type of charge of the mineral particle is crucial for determining the attraction or repulsion between mineral particles and colloidal pitch (IV). The properties of mineral particles can of course be altered by surface modifications (Solomon, Hawthorne 1983b), which will change their interactions in aqueous media with colloidal pitch and each other.

4.2.5 By mineral particles and added GGM

It is known that water-soluble galactoglucomannans (GGM) stabilises pitch sterically against electrolyte-induced aggregation in the absence of fibres (see e.g. Hannuksela, Holmbom 2004), and also to some extent in the presence of fibres (III). It was therefore of interest to determine if GGM also can diminish the interactions between mineral particles and colloidal pitch. PCC B was chosen for this study, since its interactions with pitch resulted in very hydrophobic aggregates (4.2.4).

Experiments were performed by adding scalenohedral PCC (PCC B) to wood pitch emulsions with varying concentrations of water-soluble GGM, and the interactions between the particles were studied by FCM (Fig 4.14). A very low GGM concentration, only 30 ppm, already had a noticeable effect on the interactions between the pitch and the PCC (Fig 4.14). The hydrophobicity of the pitch-PCC population with 30 ppm GGM was much lower than in samples without GGM (IV). The influence of GGM on the interactions between pitch and PCC B was seen more clearly when increasing the GGM concentration to 120 ppm, i.e. the hydrophobicity of the pitch-PCC B population decreased further (Fig 4.14). The added GGM diminished the adsorption of colloidal wood pitch onto the cationic PCC. It has previously been stated that GGM does not adsorb onto PCC (Willför et al. 2000), so the GGM should not compete with pitch for sorption on the PCC surfaces. None of the tested GGM concentrations could completely prevent the interactions between the pitch and the cationic scalenohedral PCC (IV), i.e. the PCC was always more hydrophobic than pure PCC in the presence of colloidal pitch. In unbleached TMP water in a mill, the concentration of GGM may be about nine times higher than the concentration of pitch (VI), i.e. the GGM concentration would correspond to about 1700 mg/L in these experiments. The GGM concentration in peroxide-bleached TMP water can be around two times higher than the concentration of pitch (VI), i.e. about 400 mg/L with this experimental setup.

Experiments were also performed by adding kaolin or bentonite to wood pitch emulsions with varying concentrations of GGM. The formed pitch-kaolin and pitch-bentonite populations had very similar FL3 values with 0 and 580 ppm GGM (IV), hence the GGM had no significant effect on the interactions between pitch and anionic mineral particles. It has previously been shown that kaolin can remove some carbohydrates, mostly GGM, from

unbleached TMP water (Willför et al. 2000). It was also stated that GGM has an affinity to kaolin particles, since some kaolin particles no longer sediment during centrifugation after addition of dissolved substances from spruce (Mosbye et al. 2003). However, any clear evidence of interactions between kaolin and GGM, in the presence of colloidal pitch, was not seen by FCM analysis.

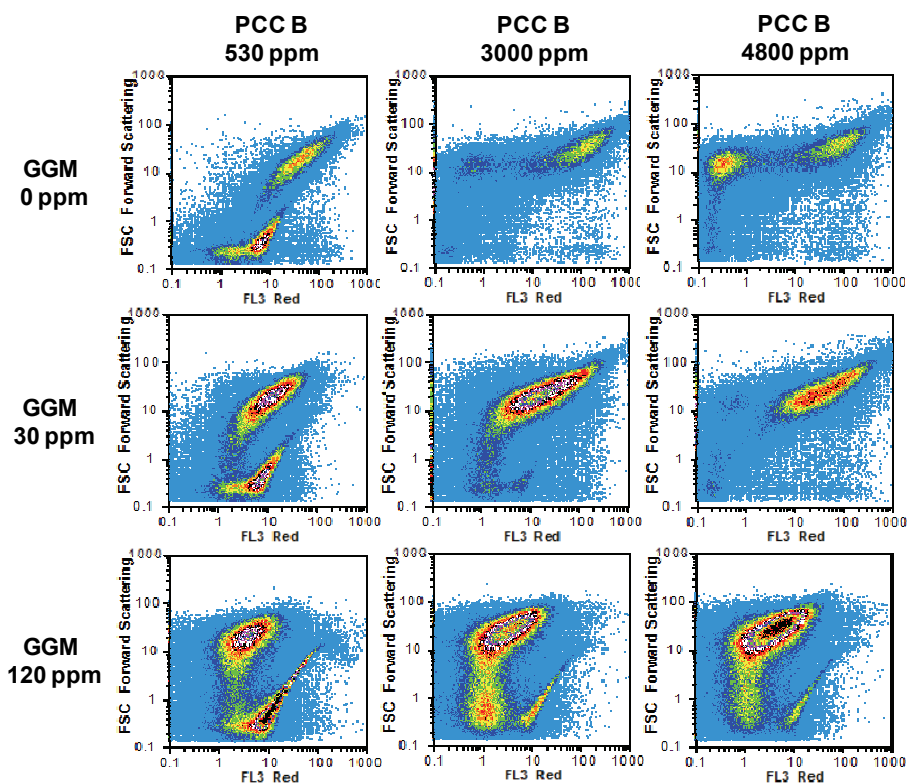


Figure 4.14 Light scattering versus hydrophobicity of colloidal pitch droplets and cationic scalenohedral PCC particles (PCC B), with 0, 30 and 120 ppm GGM, plotted in logarithmic scale (IV).

4.2.6 Summary

It was evident that interactions between colloidal pitch droplets and hydrophilic particles, such as TMP fibres or mineral particles, do occur. The main force that governs the colloidal stability of pitch in absence of steric stabilisation is repulsion of anionic carboxyl groups, which have been shown to depend on pH and electrolyte concentration. Steric stabilisation provided by water-soluble galactoglucomannans can prevent aggregation and deposition of colloidal pitch to a certain degree, although not completely, in the presence of TMP or mineral particles.

The effectiveness of cationic polymers for the aggregation of colloidal wood pitch is very dependent on pH. This indicated that low pH could be preferable in processes where effective pitch aggregation is of utmost importance.

4.3 Flotation of TMP process water

Removal of dissolved and colloidal pitch components by flotation of process waters is one of the options for reducing pitch problems in papermaking (see e.g. Tanase-Opedal 2011a). The use of froth flotation in combination with a foaming agent was recently proposed as a possible flotation setup (Zasadowski 2012b). The aim of this chapter is to assess the efficiency of froth flotation for selective removal of pitch from unbleached and peroxide-bleached TMP water at different pH.

4.3.1 Unbleached TMP water

The phase distribution of resin and fatty acids is very dependent on pH (I; II), and so is the colloidal stability of pitch (III). Froth flotations were therefore performed at different pH with a foaming agent, DoTAC, to assess the selective removal of pitch from unbleached TMP water (V). All of the added DoTAC concentrations in the experiments were well below the critical micelle concentration (Sarac, Bester-Rogac 2009).

At pH 3.5, both the RFAs and the neutral pitch substances were removed to a high extent in the flotation with 80 ppm DoTAC at 20°C (Fig 4.15). The cationic charge of DoTAC seemed to target the anionic charges of resin and fatty acids, leading to their removal from the TMP water. The RFAs were mainly attached to the neutral pitch at pH 3.5 (I; II), which meant that also the neutral pitch was removed alongside the RFAs at low pH. It is known that the anionic charge of DCS from TMP is quite low at pH 3.5 due to the protonated carboxyl groups of the dissolved and colloidal substances (Sundberg, K. et al. 1996b). Therefore, lower concentrations of a cationic coagulant are needed to achieve extensive aggregation and destabilisation of colloidal wood pitch at lower pH (III; 4.2.3).

At pH 5.1, the RFAs were still removed to a high extent, while the neutral pitch substances were more difficult to remove than at pH 3.5 (Fig 4.15). At pH 5.1, the RFAs were not associated with the colloidal pitch droplets to the same extent as at pH 3.5 (I; II; MacNeil et al. 2011), implying that some of the RFAs interacted with the DoTAC in the water phase, and not on the surface of the pitch droplets. The TMP water also contained a high concentration of water-soluble GGM (IV), which further provided steric stabilisation to the colloidal pitch. Steric stabilisation by GGM does not necessarily provide

complete colloidal stability against aggregation, especially in the presence of solid surfaces (III; IV).

At pH 7.6, the residual concentration of RFAs in the TMP water was higher than after flotations at lower pH (Fig 4.15). The increase in pH had shifted the phase distribution of RFAs from the colloidal pitch droplets further towards the water phase (I; II). 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. 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 strong agitation in the flotation cell. Pulp washing experiments have previously showed that more pitch is released from TMP at higher pH (Ekman et al. 1990; Örså et al. 1997; Holmbom 2000). This flotation setup was not effective at pH 7.6 because of the poor pitch removal and unreasonably large foam volume (V).

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 due to their solubility in water. It was recently suggested that the resin acids may form an outer shell around the colloidal pitch droplets (Lee 2011), 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 *Pinus radiata* where resin acids are abundant (Lee 2011; Lloyd et al. 1990). Resin acids have been specified as the major contributor to pitch deposition (McLean et al. 2005b).

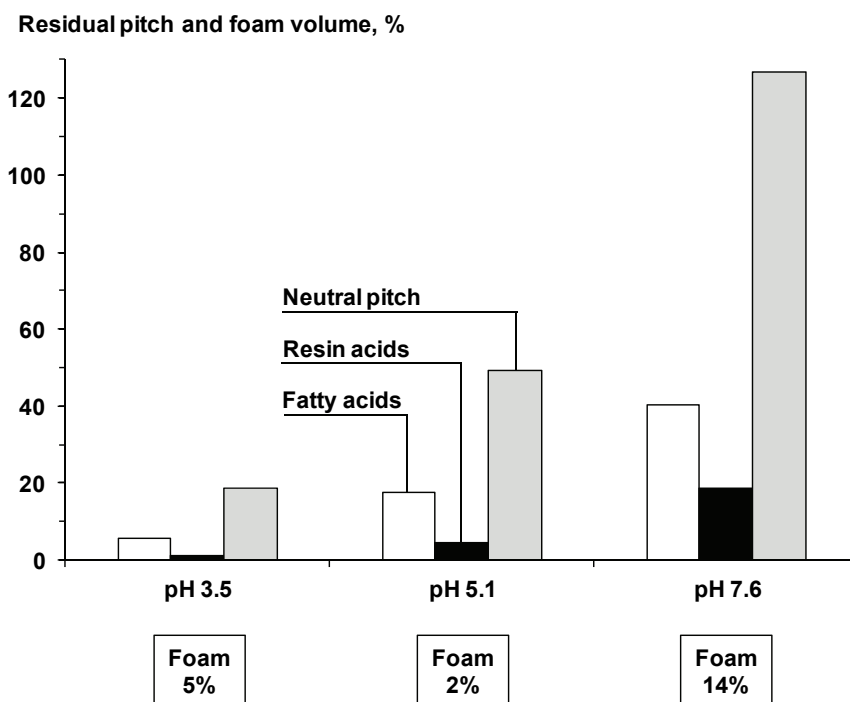


Figure 4.15 Residual pitch concentrations after flotation of unbleached TMP water, with 80 ppm DoTAC at 20 °C (V). The foam volume is expressed as a percentage of the total volume of TMP water used in the flotation.

The influence of DoTAC concentration, and increasing the temperature to 50°C, on the flotation efficiency was assessed at pH 3.5 and 5.1. At pH 5.1 with 80 ppm DoTAC, the residual concentrations of pitch components were slightly higher than after flotation performed at 20°C (Fig 4.16). Simply increasing the temperature was not enough to make the removal of pitch more efficient at pH 5.1. Lowering the pH from 5.1 to 3.5 in the flotation with 80 ppm DoTAC resulted in very low residual concentrations of both RFAs and neutral pitch (Fig 4.16), much like in the flotation at 20°C. However, at elevated temperature the high concentration of DoTAC at pH 3.5 also lead to a very large foam volume, i.e. 22% of the total TMP water volume. The experiments indicated that high DoTAC concentrations should be avoided at low pH (V). Excess of free DoTAC seemed to result in large foam volumes, which would be unacceptable for froth flotation in most industrial applications.

Experiments were therefore also conducted at 50°C with a lower DoTAC concentration at pH 5.1 and 3.5 to decrease the foam volumes. At pH 5.1, the residual concentration of resin and fatty acids was significantly higher after flotation with 40 ppm DoTAC compared to after flotation with 80 ppm (Fig 4.16). With 40 ppm DoTAC, lowering the pH from 5.1 to 3.5 once again resulted in a decrease in the residual pitch components. The lowered DoTAC concentration at pH 3.5 did result in a much smaller foam volume, but the residual pitch concentrations were significantly higher than after flotation with 80 ppm DoTAC. The results showed that efficient pitch removal can theoretically be achieved at low pH, but further optimisation is required to simultaneously avoid unreasonable large foam volumes (V). The residual concentration of water-soluble hemicelluloses and pectins in the TMP water was very high after most of the flotations (V), which concludes the high selectivity of this flotation setup. It was also found that even more pitch could be removed by the inclusion of air flow into the flotation cell during flotation (V).

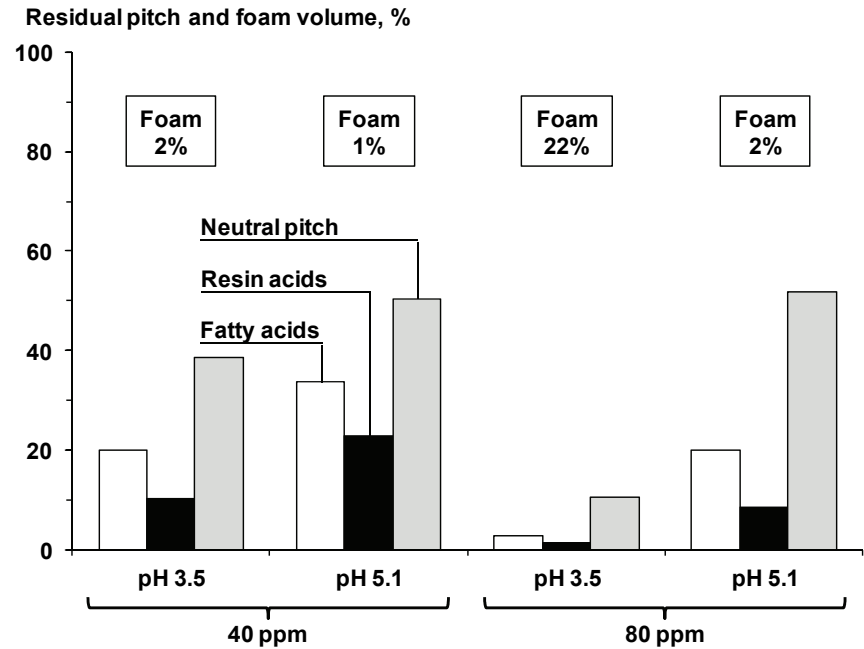


Figure 4.16 Residual pitch after flotation of unbleached TMP water, with 40 and 80 ppm DoTAC at 50°C (V).

4.3.2 Peroxide-bleached TMP water

Froth flotations were also performed with peroxide-bleached TMP water to assess if the flotation should be performed before or after peroxide bleaching in order to achieve the best removal efficiency of pitch.

Flotation at pH 7.3, with only 10 ppm DoTAC, removed the fatty acids extensively, while the residual concentration of resin acids and neutral pitch was quite high (Fig 4.17). The resin acids were not removed at neutral pH due to their high solubility in water (MacNeil et al. 2011). A significant amount of the resin acids was oxidised during the peroxide-bleaching, which further increased their solubility in water and rendered them more difficult to remove by flotation (Ekman, Holmbom 1989; Holmbom 2000; VI). The neutral pitch was more easily removed by froth flotation from peroxide-bleached TMP water compared to from unbleached TMP-water. The concentration of water-soluble GGM was much lower in peroxide-bleached TMP water (VI) than in unbleached TMP water (V). It has been shown that steric stabilisation by GGM can prevent aggregation and destabilisation of colloidal pitch (Sundberg, K. 1996a; III). The low concentration of GGM was not enough to sterically stabilise the colloidal pitch in the peroxide-bleached water. It was, however, evident that a much lower DoTAC concentrations were needed for removal of pitch from peroxide-bleached TMP water than from unbleached water.

Lowering the pH from 7.3 to 5.1 resulted in a more efficient removal of pitch from peroxide-bleached TMP water (Fig 4.17), as was the case with unbleached TMP water. The phase distribution of RFAs was shifted more towards the lipophilic pitch droplets at lower pH (I; II; MacNeil et al. 2011). These results, once again, highlight the importance of the pH-dependent phase distribution of RFAs (I; II).

At pH 3.5, the residual concentration of fatty acids was only 13%, resin acids 9%, and neutral pitch 12% after flotation (Fig 4.17). Lowering the pH resulted in a more efficient removal of pitch from peroxide-bleached TMP water, as was the case with unbleached TMP water. However, lowering the pH to 3.5 in the flotation also resulted in a significant increase in the foam volume, which was also similar to the flotations of unbleached TMP water at pH 3.5.

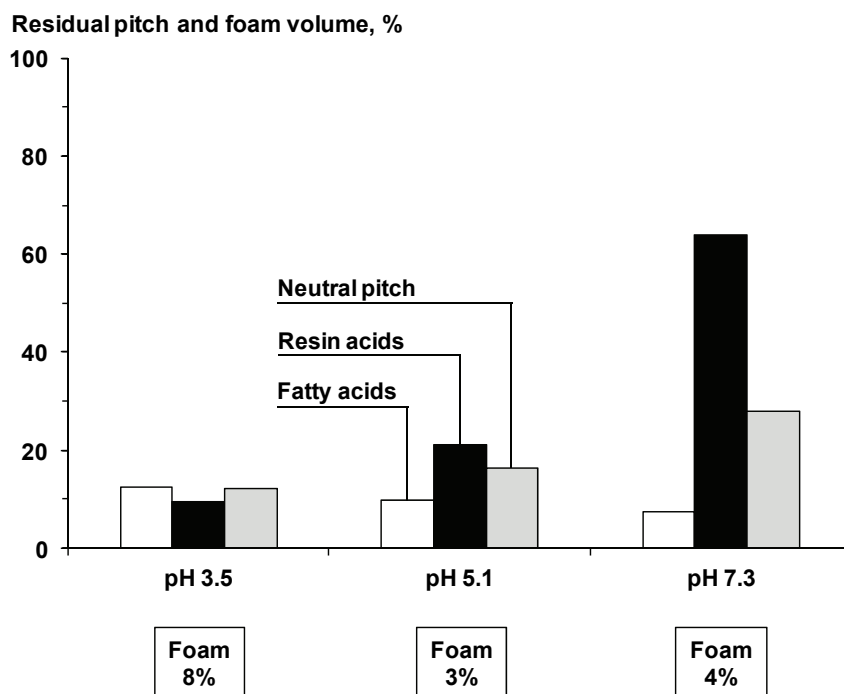


Figure 4.17 Residual pitch after flotation of peroxide-bleached TMP water, with 10 ppm DoTAC at 20°C (VI).

Flotations were also performed with 0 and 40 ppm DoTAC at 50°C, at pH 3.5 and 5.1. At both pH 3.5 and 5.1, flotation with 40 ppm DoTAC resulted in very low residual concentrations of all pitch components (Fig 4.18). The flotations even removed most of the oxidised resin acids, even though these are very soluble in water (VI). The foamability of the peroxide-bleached TMP water was higher than for the unbleached water, which resulted in larger foam volumes at pH 3.5 and 5.1 with 40 ppm DoTAC.

The residual concentrations of all pitch components were very low after the flotations, also without additions of DoTAC (Fig 4.18). The pitch was removed because of the large volume of foam formed during flotation of the peroxide-bleached water in combination with the poor colloidal stability of the pitch (VI). The foam volumes without DoTAC additions were 5-7%, i.e. still quite high compared to the flotations of unbleached TMP water (4.3.1). The foaming of the peroxide-bleached water may have been caused by residual bleaching chemicals, such as sodium silicates or by surface active

aggregates of pectic acids or other wood components that were formed during the alkaline bleaching stage.

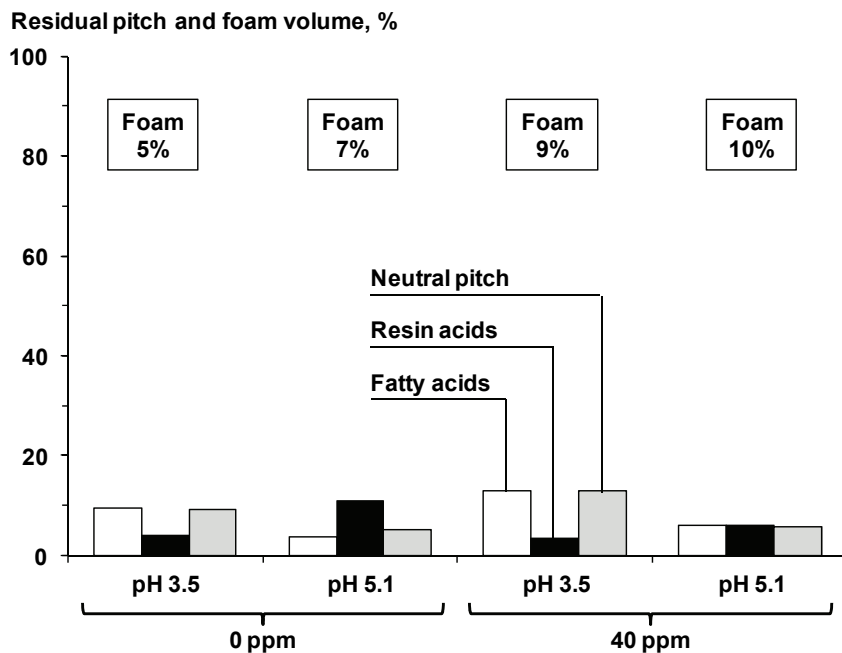


Figure 4.18 Residual pitch after flotation of peroxide-bleached TMP water, with 0 and 40 ppm DoTAC at 50 °C (VI).

4.3.3 Summary

The influence of pH on froth flotation of unbleached and peroxide-bleached TMP water with DoTAC is very significant. All pitch components are more effectively removed from unbleached and peroxide-bleached TMP water by froth flotation at acidic pH compared to flotation at neutral conditions. The carboxyl groups of resin and fatty acids are targeted by the cationic DoTAC. The amount of anionic charges of the DCS, as well as the pH-dependent phase distribution of resin and fatty acids, are crucial for optimising of the froth flotation. The dose of DoTAC should be optimised against the anionic charge of the pitch to avoid free DoTAC in the water, which leads to large foam volumes (Fig 4.19). High concentrations of water-soluble galactoglucomannans remain after the 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.

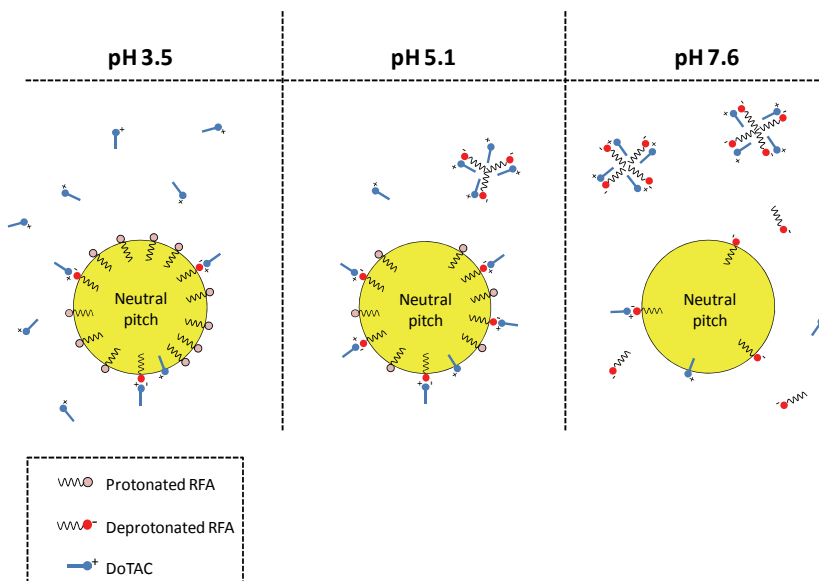


Figure 4.19 Proposed model of colloidal pitch, RFAs and DoTAC at different pH levels (V). The RFAs may have formed pre-micellar aggregates in the water phase, due to their limited solubility. A high concentration of surface active components in the water phase will cause more foaming, which was the case at pH 3.5 and 7.6.

5. CONCLUSIONS

The main objective of this work was to determine the importance of pH on the behaviour of colloidal wood pitch. The results obtained in this thesis show that pH influences the solubility of certain pitch components, the colloidal stability of pitch, the efficiency of cationic polymers for pitch aggregation, and the efficiency of pitch removal by froth flotation.

Resin and fatty acids (RFAs) are present in pitch emulsions in either colloidal or dissolved form depending primarily on pH. The fatty acids are released from the colloidal, lipophilic pitch droplets at different pH, depending on their chain length and the number of double bonds in the chain. The resin acids are released from the colloidal pitch at lower pH than fatty acids due to their bulky structure, which reduces their packing abilities in a surface layer. The release of RFAs from the pitch droplets to the water phase shifts towards higher pH in the presence of salts, while it shifts towards lower pH if the ratio of neutral pitch to RFAs is low. The dissolution and adsorption of RFAs at a sudden pH-change takes place very quickly.

Interactions between lipophilic pitch droplets and hydrophilic particles, such as TMP fibres or mineral particles, do occur. Repulsion of anionic groups, which have been shown to depend on pH and electrolyte concentration, governs the colloidal stability of pitch. Steric stabilisation provided by water-soluble galactoglucomannans can prevent aggregation and deposition of colloidal pitch to a certain degree, although not completely, in the presence of TMP or mineral particles. The effectiveness of cationic polymers for the aggregation of colloidal wood pitch is very dependent on pH. Low pH is, therefore, preferable in processes where effective pitch aggregation is desirable.

The influence of pH on froth flotation of unbleached and peroxide-bleached TMP mill water with a foaming agent is very significant. All pitch components are more effectively removed from unbleached and peroxide-bleached TMP water by froth flotation at acidic pH compared to flotation at neutral conditions. The amount of anionic charges of the pitch, as well as the pH-dependent phase distribution of resin and fatty acids, are crucial for optimising of the froth flotation. High concentrations of water-soluble galactoglucomannans remain after the flotation; hence this flotation setup removes pitch quite selectively. It is evident that industrially relevant

temperatures, slightly acidic pH, optimised dosage of DoTAC and additional air flow are the keys to selective removal of colloidal and dissolved pitch by froth flotation.

These results indicate that pitch problems could be diminished if certain papermaking processes, such as flotation and fixation, were conducted at slightly acidic conditions, rather than at neutral or alkaline conditions. These processes are more efficient since most of the dissolved RFAs are associated with the colloidal pitch. Online measurements of the pH in water streams, in combination with effective pH control, are very important in order to ensure good runnability and to avoid pitch problems.

6. REFERENCES

- Allen, L. (1975): Pitch in wood pulps, *Pulp Pap. Can.* 76(5), T139-T145.
- Allen, L. (1980): Mechanisms and control of pitch deposition in newsprint mills, *Tappi J.* 63(2), 81-87.
- Allen, L. (1988): The importance of pH in controlling metal soap deposition, *Tappi J.* 71(1), 61-64.
- Allen, L. (2000): Pitch control in pulp mills, In Back, E. and Allen, L. (ed.) *Pitch control, wood resin and deresination*, TAPPI press, Atlanta, pp. 265-287.
- Back, E. (2000): Resin in suspensions and mechanisms of its deposition, In: Back, E. and Allen, L. (ed.), *Pitch control, wood resin and deresination*, TAPPI Press, Atlanta, pp. 151-183.
- Bertaud, F., Holmbom, B., (2004): Chemical composition of earlywood and latewood in Norway spruce heartwood, sapwood, and transition zone wood, *Wood Sci. Technol.* 38(4), 245-256.
- Björklund Jansson, M., Nilvebrant, N-O. (2009): Wood extractives, In: Ek, M., Gellerstedt, G., Henriksson, G. (ed.), *Pulp and paper chemistry and technology – Wood chemistry and biotechnology*, De Gruyter, Hubert & Co, Göttingen, 147-172.
- Costa, C., Rubio, J. (2005): Deinking flotation: influence of calcium soap and surface active substances, *Miner. Eng.* 18(1), 59-64.
- Dunham, A., Tubergen, K., Govoni, S., Alfano, J. (2000): The effects of dissolved and colloidal substances on flocculation of mechanical pulps, *J. Pulp Pap. Sci.* 26(3), 95-101.
- Eklund, D., Lindström, T. (1991): *Paper chemistry – An introduction*, DT Paper Science Publications, Grankulla.
- Ekman, R. (2000): Resin during storage and in biological treatment, In: Back, E. and Allen, L. (ed.) *Pitch control, wood resin and deresination*, TAPPI press, Atlanta, pp. 185-204.

Ekman, R., Eckerman, C., Holmbom, B. (1990): Studies on the behavior of extractives in mechanical pulp suspensions, *Nord. Pulp Pap. Res. J.* 5(2), 96-103.

Ekman, R., Holmbom, B., (1989): The wood extractives in alkaline peroxide bleaching of groundwood from Norway spruce, *Nord. Pulp Pap. Res. J.* 4(3), 188-191.

Ekman, R., Holmbom, B. (2000): The chemistry of wood resin, In: Back, E. and Allen, L. (ed.) *Pitch control, wood resin and deresination*, TAPPI press, Atlanta, pp. 37-76.

Fardim, P., Holmbom, B., Ivaska, A., Karhu, J., Mortha, G., Laine, J. (2002): Critical comparison and validation of methods for determination of anionic groups in pulp fibres, *Nord. Pulp Pap. Res. J.* 17(3), 346-351.

Fengel, D., Wegener, G. (1984): *Wood – Chemistry, ultrastructure, reactions*, De Gruyter, Berlin.

Fox, M., Whitesell, J. (1997): *Organic chemistry* (second edition), Jones and Bartlett Publishers International, London.

Gantenbein, D., Schoelkopf, J., Gane, P., Matthews, P. (2010): Influence of pH on the adsorption of dissolved and colloidal substances in a thermo-mechanical pulp filtrate onto talc, *Nord. Pulp Pap. Res. J.* 25(3), 288-299.

Gantenbein, D., Schoelkopf, J., Matthews, P., and Gane, P. (2012): The use of porous high surface area calcium carbonate for the adsorption of dissolved and colloidal substances from thermo mechanical pulp filtrates, *Nord. Pulp Pap. Res. J.* 27(3), 631-638.

Gellerstedt, G. (2009): Mechanical pulping chemistry, In: Ek, M., Gellerstedt, G., Henriksson, G. (ed.), *Pulp and paper chemistry and technology – Pulping chemistry and technology*, De Gruyter, Hubert & Co, Göttingen, 35-56.

Granhölm, K. (2011): Sorption/desorption reactions of metal ions with pulp, PhD thesis, Åbo Akademi University, Turku, Finland.

Hannuksela, T., Holmbom, B. (2004): Stabilization of wood-resin emulsions by dissolved galactoglucomannans and galactomannans, *J. Pulp Pap. Sci.* 30(6), 159-164.

Hassler, T. (1988): Pitch deposition in papermaking and the function of pitch-control agents, *Tappi J.* 71(6), 195-201.

Heikkilä, R., Deamer, D., Cornwell, D. (1970): Solution of fatty acids from monolayers spread at the air-water interface: identification of phase transformations and the estimation of surface charge, *J. Lipid Res.* 11(3), 195-200.

Holmbom, B. (2000): Resin reactions and deresination in bleaching, In: Back, E. and Allen, L. (ed.) *Pitch control, wood resin and deresination*, TAPPI press, Atlanta, pp. 231-244.

Holmbom, B., Hannuksela, T., Viitikko, K. (2004): Seasonal variations in spruce wood and TMP water, *Eight European Workshop on Lignocellulosics and Pulp*, Riga, Latvia, August 22-25, pp. 97-100.

Holmbom, B., Pranovich, A., Sundberg, A., Buchert, J. (2000): Charged groups in wood and mechanical pulps, In: Kennedy, J., Philips, G. and Williams, P. (ed.), *Cellulosic pulps, fibres and materials*, Woodhead Publishing Ltd., Cambridge, pp. 109-119.

Holmbom, B., Sundberg, A. (2003): Dissolved and colloidal substances accumulating in papermaking process waters, *Wochenblatt Papierfabrikation* 131(21), 1305-1311.

Höglund, H. (2009): Mechanical pulping, In: Ek, M., Gellerstedt, G., Henriksson, G. (ed.), *Pulp and paper chemistry and technology – Pulping chemistry and technology*, De Gruyter, Hubert & Co, Göttingen, 57-90.

Jankowsky, R., Friebe, M., Noll, B., Johannsen, B. (1999): Determination of dissociation constants of ^{99m}Techneium radiopharmaceuticals by capillary electrophoresis, *J. Chromatogr. A* 833(1), 83-96.

Johnsen, I., Lenes, M., Magnusson, L. (2004): Stabilization of colloidal wood resin by dissolved material from TMP and DIP, *Nord. Pulp Pap. Res. J.* 19(1), 22-28.

Kappel, J. (1999): *Mechanical pulps: from wood to bleached pulp*, Tappi Press, Atlanta.

Kangas, H., Kleen, M. (2004): Surface chemical and morphological properties of mechanical pulp fines, *Nord. Pulp Pap. Res. J.* 19(2), 191-199.

Kanicky, J., Poniatowski, A., Mehta, N., Shah, D. (2000): Cooperativity among molecules at interfaces in relation to various technological processes: Effects of chain length on pK_a of fatty acid salt solutions, *Langmuir* 16(1), 172-177.

Kanicky, J., Shah, D. (2002): Effect of degree, type, and position of unsaturation on the pK_a of long-chain fatty acids, *J. Colloid Interface Sci.* 256(1), 201-207.

Kanicky, J., Shah, D. (2003): Effect of premicellar aggregation on the pK_a of fatty acid soap solutions, *Langmuir* 19(6), 2034-2038.

Kekkonen, J., Stenius, P. (1999): Interactions of oxide surfaces with dissolved and colloidal substances released in mechanical pulping, *Nord. Pulp Pap. Res. J.* 14(4), 300-309.

Koljonen, K., Österberg, M., Johansson, L.-S., Stenius, P. (2003): Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM, *Colloids Surf. A* 228 (1-3): 143-158.

Korpela, A. (2006): Removal of resin from mechanical pulps by selective flotation: mechanisms of resin flotation and yield loss of fibers, *J. Wood Chem. Technol.* 26(2): 175-186.

Lee, R. (2011): The stability of wood resin colloids in paper manufacture, PhD thesis, University of Tasmania, Hobart, Tasmania, Australia.

Leiviskä, T., Sarpola, A., Tanskanen, J. (2012): Removal of lipophilic extractives from debarking wastewater by adsorption on kaolin or enhanced coagulation with chitosan and kaolin, *Appl. Clay Sci.* 61, 22-28.

Lindström, M., Ödberg, L., Stenius, P. (1988): Resin and fatty acids in kraft pulp washing: physical state, colloid stability and washability, *Nord. Pulp Pap. Res. J.* 3 (2), 100-106.

Lindström, T. (1991): Electrokinetics in the papermaking industry, In: Roberts, J. (ed.) *Paper Chemistry*, Blackie & Son Ltd., Glasgow, pp. 25-43.

- Lloyd, J., Deacon, N., Horne, C. (1990): The influence of pulping and washing conditions on the resin content of radiata pine mechanical pulps, *Appita J.* 43(6), 429-434.
- MacNeil, D., Sundberg, A., Vähäsalo, L., Holmbom, B. (2011): Effect of calcium on the phase distribution of resin and fatty acids in pitch emulsions, *J. Disp. Sci. Technol.* 32(2), 269-276.
- Maher, L., Stack, K., McLean, D., Richardson, D. (2007): Adsorption behaviour of cationic fixatives and their effect on pitch deposition, *Appita J.* 60(2), 112-119, 128.
- McLean, D., Vercoe, D., Stack, K., Richardson, D. (2005a): The colloidal pK_a of lipophilic extractives commonly found in *Pinus radiata*, *Appita J.* 58(5), 362-366.
- McLean, D., Stack, K., Richardson, D. (2005b): The effect of wood extractives composition, pH and temperature on pitch deposition, *Appita J.* 58(1), 52-56.
- McLean, D., Stack, K., Richardson, D. (2010): Evaluation of cationic polymers to control pitch deposition, *Appita J.* 63(3), 199-205.
- Miyaniishi, T., Kamijo, Y., Ono, H. (2000): Adsorption of anionic dissolved and colloidal substances onto calcium carbonate fillers, *Tappi J.* 83(7).
- Mosbye, J., Holtermann, M., Laine, J., Moe, S. (2003): Interactions between model colloidal wood resin, fillers and dissolved substances, *Nord. Pulp Pap. Res. J.* 18(2), 194-199.
- Mosbye, J., Moe, S., Laine, J. (2002): The charge and chemical composition of fines in mechanical pulp, *Nord. Pulp Pap. Res. J.* 17(3), 352-356.
- Mosbye, J., Richardson, D., Parsons, T. (2008): Solving pitch deposit problems on paper machines using mechanical pulp, 62nd Appita Annual Conference and Exhibition, April 20-23, Rotorua, New Zealand, pp. 185-189.
- Negro, C., Blanco, A., Saarimaa, V., Tijero, J. (2005): Optimization of pitch removal by dissolved air flotation in a eucalyptus kraft mill, *Sep. Sci. Technol.* 40(5), 1129-1143.

Neimo, L. (1999): Papermaking chemistry, Fapet Oy, Gummerus Printing, Jyväskylä.

Nicke, R., Pensold, S., Tappe, M., Hartmann, H.-J. (1992): Polydiallyldimethylammonium-chlorid als flockungsmittel, Wochenbl. Papierfabr. 120(14), 559-564.

Nurmi, M., Eklund, D. (2000): Effect of cationic polyacrylamide on colloidal wood resin, Pap. Puu 82(5): 331-334.

Nurmi, M., Wallin, S., Eklund, D. (2006): The effect of molar mass and charge density of cationic polyacrylamide on the flocculation of dissolved and colloidal substances in thermomechanical pulp, J. Pulp Pap. Sci. 32(1): 43-46.

Nurmi, M., Westerholm, M., Eklund, D. (2004): Factors influencing the flocculation of dissolved and colloidal substances in a thermomechanical pulp water, J. Pulp Pap. Sci. 30(2), 41-44.

Nylund, J., Byman-Fagerholm, H., Rosenholm, J. (1993): Physico-chemical characterization of colloidal material in mechanical pulp, Nord. Pulp Pap. Res. J. 8(2), 280-283.

Nylund, J., Lagus, O., Rosenholm, J. (1995): Dissolved and colloidal substances from mechanical pulp suspensions – stability and flocculation behaviour, Colloids Surf. A 104(2-3), 137-146.

Nylund, J., Sundberg, A., Sundberg, K. (2007): Dissolved and colloidal substances from a mechanical pulp suspension - Interactions influencing the sterical stability, Colloids Surf. A., 301 (1-3): 335-340.

Nyrén, V., Back, E. (1958): Ionization constant, solubility product, and solubility of abietic and dehydroabietic acid, Acta Chem. Scand. 12: 1516-1520.

Otero, D., Sundberg, K., Blanco, A., Negro, C., Tijero, J., Holmbom, B. (2000): Effects of polysaccharides on pitch deposition, Nord. Pulp Pap. Res. J. 15(5): 607-613.

Palonen, H., Stenius, P., Ström, G. (1982): Surfactant behavior of wood resin components: The solubility of rosin and fatty acid soaps in water and in salt solutions, Sven. Papperstidn. 85(12), R93-R99.

Pranovich, A., Eckerman, C., Holmbom, B. (2002): Determination of methanol released from wood and mechanical pulp by headspace solid-phase microextraction, *J. Pulp Pap. Sci.* 28(6), 199-203.

Pranovich, A., Sundberg, K., Holmbom, B. (2003): Chemical changes in thermomechanical pulp at alkaline conditions, *J. Wood Chem. Technol.* 23(1), 89-112.

Pranovich, A., Reunanen, M., Sjöholm, R., Holmbom, B. (2005): Dissolved lignin and other aromatic substances in thermomechanical pulp waters, *J. Wood Chem. Technol.* 25 (3), 109-132.

Puro, L., Kallioinen, M., Mänttari, M., Nyström, M. (2011): Evaluation of behaviour and fouling potential of wood extractives in ultrafiltration of pulp and paper mill process water, *J. Membr. Sci.* 368(1-2), 150-158.

Qin, M., Hannuksela, T., Holmbom, B. (2003): Physicochemical characterisation of TMP resin and related model mixtures, *Colloids Surf. A* 221(1-3), 243-254.

Qin, M., Hannuksela, T., Holmbom, B. (2004): Deposition tendency of TMP resin and related model mixtures, *J. Pulp Pap. Sci.* 30(10), 279-283.

Richardson, D., Grubb, M. (2004): Extractives removal from newsprint mill process waters by dissolved air flotation, *Proc. 58th Appita Ann. Conf.*, Canberra, Australia, pp. 79-84.

Richardson, D., Lee, R., Stack, K., Lewis, T., Garnier, G. (2012): Process factors affecting colloid stability and deposit formation in manufacture of newsprint from TMP and recycled fibre, *Appita J.* 65(4), 323-330.

Rogan, K. (1994): Adsorption of oleic acid and triolein onto various minerals and surface treated minerals, *Colloid Polym. Sci.* 272(1), 82-98.

Rundlöf, M. (2002): Interaction of dissolved and colloidal substances with fines of mechanical pulp – Influence on sheet properties and basic aspects of adhesion, PhD thesis, Mid Sweden University, Sundsvall.

Rundlöf, M., Eriksson, M., Ström, H., Wågberg, L. (2002): Effect of mannanase and lipase on the properties of colloidal wood extractives and their interaction with mechanical pulp fines, *Cellulose* 9(2), 127-137.

Saarimaa, V., Sundberg, A., Holmbom, B., Blanco, A., Negro, C., Fuente, E. (2006a): Purification of peroxide-bleached TMP water by dissolved air flotation, *Tappi J.* 5(5), 15-21.

Saarimaa, V., Sundberg, A., Holmbom, B., Blanco, A., Fuente, E., Negro, C. (2006b): Monitoring of dissolved air flotation by focused beam reflectance measurements, *Ind. Eng. Chem. Res.* 45(1), 7256-7263.

Saarimaa, V., Vähäsalo, L., Sundberg, A., Pranovich, A., Holmbom, B., Svedman, M., Örså, F. (2006c): Influence of pectic acids on aggregation and deposition of colloidal pitch, *Nord. Pulp Pap. Res. J.* 21(5), 93-99.

Sarac, B., Bester-Rogac, M. (2009): Temperature and salt-induced micellization of dodecyltrimethylammonium chloride in aqueous solution: A thermodynamic study, *J. Colloid Interf. Sci.* 338(1), 216-221.

Scott, W. (1996): Surface and colloid science concepts important to paper-making chemistry, In: Scott, W. (ed.), *Principles of Wet End Chemistry*, TAPPI Press, Atlanta, pp. 21-32.

Sihvonen, A-L., Sundberg, K., Sundberg, A., Holmbom, B. (1998): Stability and deposition tendency of colloidal wood resin, *Nord. Pulp Pap. Res. J.* 13(1), 64-67.

Sitholé, B. (2000): Analysis of resin deposits, In: Back, E. and Allen, L. (ed.), *Pitch control, wood resin and deresination*, TAPPI Press, Atlanta, pp. 289-306.

Sjöström, E. (1981): *Wood chemistry – fundamentals and applications*, Academic Press Inc., New York.

Solomon, D., Hawthorne, D. (1983a): Structures and chemical activity of silicate minerals, fillers, and pigments, In: Solomon, D., Hawthorne, D. (ed.), *Chemistry of pigments and fillers*, John Wiley & sons, New York, pp. 1-50.

Solomon, D., Hawthorne, D. (1983b): Surface modification of pigments and fillers, In: Solomon, D., Hawthorne, D. (ed.), *Chemistry of pigments and fillers*, John Wiley & sons, New York, pp. 108-178.

Stack, K., Lee, R., Zhang, J., Lewis, T., Garnier, G., Richardson, D. (2011): Colloidal and deposition behaviour of pinus radiata extractives and model

colloid systems, 16th International Symposium on Wood, Fiber and Pulp Chemistry, June 8-10, Tianjin, China, pp. 1243-1248.

Stenius, P. (2000): Forest products chemistry, Fapet Oy, Gummerus Printing, Jyväskylä.

Ström, G., Barla, P., Stenius, P. (1985): The formation of polyelectrolyte complexes between Pine xylan and cationic polymers, *Colloid. Surf.* 13(2-3), 193-207.

Ström, G. (2000): Physico-chemical properties and surfactant behaviour, In: Back, E. and Allen, L. (ed.), *Pitch control, wood resin and deresination*, TAPPI Press, Atlanta, pp. 139-149.

Ström, G., Stenius, P., Lindström, M., Ödberg, L. (1990): Surface chemical aspects of the behavior of soaps in pulp washing, *Nord. Pulp Pap. Res. J.* 5(1), 44-51.

Sundberg, A., Ekman, R., Holmbom, B., Grönfors, H. (1994): Interactions of cationic polymers with components in thermomechanical pulp suspensions, *Pap. Puu* 76(9), 593-598.

Sundberg, A., Pranovich, A., Holmbom, B. (2000): Distribution of anionic groups in thermomechanical pulp (TMP) suspensions, *J. Wood Chem. Technol.* 20(1), 71-92.

Sundberg, A., Pranovich, A., Holmbom, B. (2003): Chemical characterization of various types of mechanical pulp fines, *J. Pulp Pap. Sci.* 29(5), 173-178.

Sundberg, A., Sundberg, K., Lillandt, C., Holmbom, B. (1996): Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography, *Nord. Pulp Pap. Res. J.* 11(4), 216-219.

Sundberg, K., Holmbom, B. (1997): Destabilization of colloidal wood resin caused by cellulosic fibers in thermomechanical pulp suspensions, *Pap. Puu* 79(1), 50-54.

Sundberg, K., Thornton, J., Ekman, R., Holmbom, B. (1994a): Interactions between simple electrolytes and dissolved and colloidal substances in mechanical pulp, *Nord. Pulp Pap. Res. J.* 9(2), 125-128.

- Sundberg, K., Thornton, J., Pettersson, C., Holmbom, B., Ekman, R. (1994b): Calcium-induced aggregation of dissolved and colloidal substances in mechanical pulp suspensions, *J. Pulp Pap. Sci.* 20(11), J317-J322.
- Sundberg, K., Thornton, J., Holmbom, B., Ekman, R. (1996a): Effects of wood polysaccharides on the stability of colloidal wood resin, *J. Pulp Pap. Sci.* 22(7), J226-J230.
- Sundberg, K., Pettersson, C., Eckerman, C., Holmbom, B. (1996b): Preparation and properties of a model dispersion of colloidal wood resin from Norway spruce, *J. Pulp Pap. Sci.* 22(7), J248-J252.
- Sundholm, J. (1999): Papermaking science and technology - Mechanical pulping, Fapet Oy, Helsinki.
- Tanase-Opedal, M., Stenius, P., Johansson, L. (2011a): Review: Colloidal stability and removal of extractives from process water in thermomechanical pulping, *Nord. Pulp Pap. Res. J.* 26(3), 248-257.
- Tanase-Opedal, M., Stenius, P., Johansson, L., Hill, J., Sandberg, C. (2011b): Removal of dissolved and colloidal substances in water from compressive pre-treatment of chips using dissolved air flotation. Pilot trial, *Nord. Pulp Pap. Res. J.* 26(4), 364-371.
- Teeri, T., Henriksson, G. (2009): Enzymes degrading wood components, In: Ek, M., Gellerstedt, G., Henriksson, G. (ed.), *Pulp and paper chemistry and technology – Wood chemistry and biotechnology*, De Gruyter, Hubert & Co, Göttingen, 245-271.
- Thornton, J., Ekman, R., Holmbom, B., Örså, F. (1994): Polysaccharides dissolved from Norway spruce in thermomechanical pulping and peroxide bleaching, *J. Wood Chem. Technol.* 14(2), 159-175.
- van Olphen, H. (1955): Forces between suspended bentonite particles, *Clay & Clay Miner.* 4(1), 204-224.
- Vercoe, D. (2004): Study of the interactions leading to wood resin deposition, PhD thesis, University of Tasmania, Hobart, Tasmania, Australia
- Vähäsalo, L., Degerth, R., Holmbom, B. (2003): Use of flow cytometry in wet end research, *Pap. Tech.* 44(1), 45-49.

Vähäsalo, L., Holmbom, B. (2005): Factors affecting white pitch deposition, Nord. Pulp Pap. Res. J. 20(2), 164-168.

Welkener, U., Hassler, T., McDermott, M. (1993): The effect of furnish components on depositability of pitch and stickies, Nord. Pulp Pap. Res. J. 8(1), 223-225, 232.

Werkelin, J., Skrifvars, B.-J., Hupa, M. (2005): Ash-forming elements in four Scandinavian wood species. Part 1: summer harvest, Biomass Bioenerg. 29(6), 451-466.

Willför, S., Pranovich, A., Tamminen, T., Puls, J., Laine, C., Suurnäkki, A., Saake, B., Uotila, K., Simolin, H., Hemming, J., Holmbom, B. (2009): Carbohydrate analysis of plant materials with uronic acid-containing polysaccharides – A comparison between different hydrolysis and subsequent chromatographic analytical techniques. Ind. Crops Prod. 29(2-3), 571-580.

Willför, S., Sundberg, A., Sihvonen, A.-L., Holmbom, B. (2000): Interactions between fillers and dissolved and colloidal substances from TMP, Pap. Puu 82(6), 398-402.

Wu, N., Hubbe, M., Rojas, O., Park, S. (2010): Permeation of a cationic polyelectrolyte into meso-porous silica, Part 1 - factors affecting changes in streaming potential, Colloids Surf. A 364(1-3), 1-6.

Wågberg, L., Åsell, I. (1995): The action of cationic polymers in the fixation of dissolved and colloidal substances, Colloids Surf. A 104(2-3), 169-184.

Wågberg, L., Ödberg, L. (1991): The action of cationic polyelectrolytes used for the fixation of dissolved and colloidal substances, Nord. Pulp Pap. Res. J. 6(3), 127-135.

Xu, C. (2008): Physicochemical properties of water-soluble spruce galactoglucomannans, PhD thesis, Åbo Akademi, Turku, Finland.

Zasadowski, D., Hedenström, E., Edlund, H., Norgren, M. (2012a): Removal of lipophilic extractives and manganese ions from spruce TMP waters in a customized flotation cell, BioRes. 7(2), 2376-2392.

Zasadowski, D., Hedenström, E., Edlund, H., Norgren, M. (2012b): Use of a Voith flotation cell for removal of lipophilic extractives and Mn ions from spruce thermomechanical pulping process waters, *BioRes.* 7(3), 2784-2798.

Ödberg, L., Forsberg, S., McBride, G., Persson, M., Stenius, P., Ström, G. (1985): Surfactant behavior of wood resin components – Part 2. Solubilization in micelles of rosin and fatty acids, *Svensk Papperstidn.* 88(12), R118-R125.

Örså, F., Holmbom, B. (1994): A convenient method for the determination of wood extractives in papermaking process waters and effluents, *J. Pulp Pap. Sci.* 20(12), J361-J366.

Örså, F., Holmbom, B., Thornton, J. (1997): Dissolution and dispersion of spruce wood components into hot water, *Wood Sci. Technol.* 31(4), 279-290.

