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Thesis for the degree of
philosophiae doctor
Faculty of Natural Science and Technology
Department of Chemical Engineering

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ABSTRACT

The main abjectives of this work were to evaluate the extent to which extractives in wood chips for mechanical pulping are released into process water during compressive pre-treatment before refining and to develop a method to remove the released extractives from the process water.

In thermomechanical pulping, pre-treatments based on a high compression ratio and high temperature, are used to reduce the amount of extractives in wood chips of different raw materials before refining. One objective of this study was to evaluate the removal of extractives from the wood chips during compressive pre-treatment, in an Impressafiner by determining mass balance of extractives around a mill scale Impressafiner installation. The mass balance showed that it was possible to remove up to 15% of extractives before the refining process. Thus one advantage of using an Impressafiner is that removal of dispersed extractives can be done with little loss of fibres, from a small concentrated water stream.

Handling of this water is important in order to avoid that the extractives enter the effluent treatment or reach undesirable levels in the process water. Thus the solubility, colloidal stability and flocculation of the extractives in the pressate water was studied. The objective was to obtain a better understanding of the effects of cationic polyelectrolytes on the stability of colloidal extractives in the pressate water from Impressafiner. A high charge density and low molecular mass polymer (poly-DADMAC), a high molecular mass and low charge density polymer (C-PAM) and combination of the polymers (mass ratio 1:1) were used. It was found that these polymers efficiently flocculate colloidal extractives present in the process water via two different flocculation mechanisms: charge neutralization and bridging flocculation.

Extractives which are removed from the process water have to be taken care of in an economical way. They have to be brought into a form making it possible to remove them from the process water before the water is sent to the effluent treatment or before the water is reused in the mill. In that respect, the extent to which the extractives are present in either dissolved, colloidal or bound to fibres is important. In this work, Dissolved Air Flotation (DAF) was used to remove the flocculated extractives from Impressafiner process water. For comparison, laboratory experiments were also conducted on water from chip washer. It was shown in both laboratory and pilot scale that by using DAF in combination with flocculation of the extractives with polyelectrolyte the colloidal and fibre bound extractives could be removed from the process water with a removal efficiency of 80-90%, with equal efficiency for the Impressafiner and chip washer waters.

The results attained in the thesis strongly suggest that by using a compressive pre-treatment method of the wood chips is possible to remove a substantial fraction of extractives before the refining process. A larger fraction of the more toxic extractive components, resin acids, than of fatty acids were removed. Further, this study emphasizes the importance of the polymer properties for their floccculation efficiency of colloidal extractives present in process water. The results also show that Dissolved Air Flotation is a convenient method to remove flocculated extractives from process water.

PREFACE

This thesis is submitted in partial fulfilment of the PhD degree at the Norwegian University of Science and Technology. The work has been carried out at the Paper and Fibre Research Institute (PFI) and the Department of Chemical Engineering at the Norwegian University of Science and Technology (NTNU). Professor emeritus Per Stenius, Professor Øyvind Gregersen, Lars Johansson (PFI) and Jan Hill (Norske Skog) have been supervising this work.

The work in this study is a part of the Norske Skog project "Energy-effective production of mechanical pulp by targeted treatment of extractives and selective fibre wall weakening". The doctoral study was funded by Research Council of Norway, Norske Skog and Andritz.

This thesis summarizes the following journal articles, referred to as **Paper I - V** in the text:

I. Tanase M., Stenius P., Johansson L., Hill J. and Sandberg C. (2010): Mass balance of lipophilic extractives around Impressafiner in mill and pilot scale, *Nordic Pulp and Paper Research Journal* 25(2), 162.

II. Opedal Tanase M., Stenius P., Johansson L. and Hill J. (2010): Flocculation of colloidal wood extractives in process water from precompression of chips in thermomechanical pulping, *Nordic Pulp and Paper Research Journal,* accepted.

III. Opedal Tanase M., Stenius P., Gregersen Ø., Johansson L. and Hill J. (2011): Removal of dissolved and colloidal substances from TMP process water using Dissolved Air Flotation. Laboratory tests, *Nordic Pulp and Paper Research Journal,* accepted.

IV. Opedal Tanase M., Stenius P., Johansson L., Hill J. and Sandberg C. (2011): Removal of dissolved and colloidal substances from compressive pre-treatment of chips using Dissolved Air Flotation. Pilot trial, *Nordic Pulp and Paper Research Journal,* submitted.

V. Opedal Tanase M., Stenius P., Johansson L. (2011): Review: Colloidal stability and removal of extractives from process water in thermomechanical pulping, *Nordic Pulp and Paper Research Journal,* submitted.

The planning of the mill trial in **Paper I** was done by the author and co-authors. The pilot trial in **Paper I** was done by one co-author. The experimental work in **Paper I** and the writting of the paper was done by the author. In **Paper II** the author planned and performed all the experiments. The interpretation of the results and the writting of the paper have been done by the author. The author's contribution to **Paper III** was planning, experimental work, interpretation of the reuslts and writting of the paper. The planning and experimental work in **Paper IV** was done by the outhor and one co-author. The interpretation of the results and writting of the paper was done by the author. **Paper V** have been written by the author.

Related publications

1. Tanase M., Stenius P., Johansson L. and Hill J. (2008): Removal of resin during pre-treatment of softwood chips, Oral presentation, *6th Fundamental Mechanical Pulp Research Seminar*, Espoo, Finland.

2. Tanase M., Stenius P., Johansson L., Hill J. and Sandberg C. (2009): Mass balance of extractives around Impressafiner in mill and pilot scale (Proceeding), Oral presentation, *International Mechanical Pulping Conference*, Sundsvall, Sweden.

3. Tanase M., Stenius P., Gregersen Ø., Johansson L. and Hill J. (2010): Removal of extractives from TMP process water using Dissolved Air Flotation (Proceeding), Oral presentation, *7th International Seminar of Fundamental Mechanical Pulp Research*, Nanjing, China.

4. Tanase M. (2010): Fra kostnad til fremtidig ressurs: Fjerning av ekstraktiver fra prosessvann, Oral presentation given at *Fremitidens produkter og produksjonsprosesser for norsk treforedlingsindustri - refleksjon om fremtid, utvikling og lonnsomhet,* Trondheim, Norway.

ACKNOWLEDGEMENTS

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Jan Hill, Norske Skog is acknowledged for interesting discussions during our project meetings and for valuable comments on my papers.

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All the engineers and researchers from PFI, PhD colleagues from NTNU are acknowledged for creating a nice working environment and good cooperation. Especially, I would like to thank Ingebjørg Leirset (PFI) and Anne Reitan (PFI) for all the help during my work and for nice discussions between the experimental work. Thank you, Sara for helping me when was needed.

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My family and friends are acknowledged for their encouragement and for always supporting me.

Finally, my beloved husband Nils, you attain my warmest thanks for your support, patience and love. *Du er alt for meg!*

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1
INTRODUCTION

1.1 Background

Mechanical pulping creates opening of the wood cell structure allowing the release of organic substances into the process water. Due to the environmental regulations more and more paper mills have increased the closure of their water circuit, implying increased recirculation of the process water. As result, the process water and effluents are enriched with a large number of detrimental substances, mainly organic substances, which interfere with the papermaking system. Especially extractives released into the process water create problems. The extractives tend to agglomerate and to form deposits which lead to runnability problems and uneven paper quality.

Treatment of different process water streams is important in order to reduce the concentration of dissolved and colloidal substances in the effluent treatment and in the process water. A general understanding of the different methods used to remove detrimental substances from circulating in the white water system and reduce deposition problems is thus required. Knowledge of how the dissolved and colloidal substances interact with different polymers is necessary for choosing the optimum method for removing detrimental substances from the process water.

During the thermomechanical pulping (TMP) process the pH varies substantially between different stages. For example, the process conditions during alkaline peroxide bleaching (especially the high pH) affect the amount and composition of the dissolved and colloidal substances released from the fibres into the aqueous phase. Thus, removal of detrimental substances (e.g. extractives) from the process water in the beginning of the TMP process is essential in order to improve paper machine efficiency and to avoid that the extractives accumulate in the process water (pitch problems).

1.2 Aim of this work

The main objective of this study was to investigate the possibility to remove extractives released from wood chips by using a compressive pre-treatment, such as an Impressafiner. Three different raw materials were studied in our trials: Loblolly pine, White spruce and Norway spruce. The study was particularly focused on the effect of cationic polymers on the interactions with dissolved and colloidal substances in the pressate water from an Impressafiner.

A further objective was to examine to what extent flocculated dissolved and colloidal substances could be removed from the process water by using a laboratory scale dissolved air flotation unit. The study has particularly focused on two TMP process water streams with high concentration of organic substances: Impressafiner pressate water and process water from chip washing.

Based on the laboratory results, a pilot dissolved air flotation trial was conducted for assesing the potential benefits of DAF in mill scale. The work was done using Impressafiner pressate water, directly at the mill site. Furthemore, the effect of pH and temperature of the Impressafiner pressate water on the efficiency of DAF were studied.

1.3 Outline of the thesis

This thesis comprises results from papers that have been published or submitted for publication in journals (referred to as **Paper I - V**, see pp.55).

Chapter 1. Introduction

Chapter 2 is a review of relevant literature covering the following topics: the TMP proces, dissolved air flotation and dissolved and colloidal substances.

Chapter 3 gives an overview of the experimental methods. These methods are also described in Papers I - IV.

Chapter 4 summarizes the papers

Chapter 5 presents the overall conclusions of this work.

CHAPTER
2
BACKGROUND

2.1 Thermomechanical pulping process

2.1.1 Thermomechanical pulping

The thermomechanical pulp process (TMP) was developed in the 1960's and involves disc refining at elevated pressure and temperature. Today the TMP process is the dominating process for production of pulp for wood-containing paper. Softwood is the predominant raw material for mechanical pulping. A typical TMP production line is represented schematically in *Figure 2.1*.

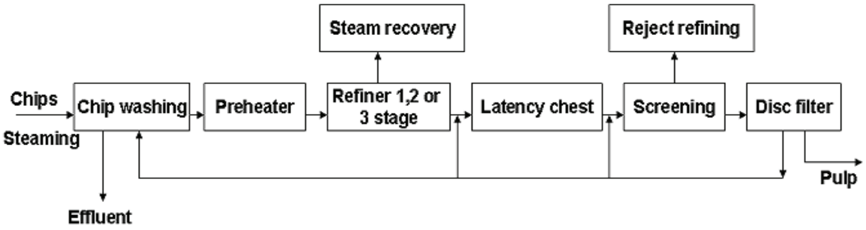

Figure 2.1: Typical TMP production line.

The wood chips are steamed atmospherically at 100°C and then washed in hot water, in the chip washer. This treatment provides a thermal softening of the wood structure and removes air and sand from the chips. The chips are preheated at a pressure of approximately 1.5-2 bar for a few minutes. The primary refining takes place at high pressure (3-5 bar) and temperature (140-160°C) at a consistency of approximately 40-50%. After the steam recovery, the pulp is blown to the second stage refiner. This refiner may be operated pressurized or atmospherically. In some cases refining is done in three stages. After refining, the pulp is diluted with water (approx. 3% consistency) and subjected to gentle agitation in an atmospheric latency chest at 20°C. This latency treatment releases tensions in the fibres allowing them to straighten. After the latency treatment, the pulp is screened. The screen reject is sent to a separate reject refiner and the pulp is sent to the disc filter or a screw press. The disc filter removes a large volume of liquid and then the pulp is further dewatered to a high consistency on a press. This water is rich in dissolved and colloidal substances. Without this wash press increasing closure of water the loops, dissolved and colloidal substances would build up in the paper machine, creating runnability problems.

2.1.2 Mechanical pre-treatment of wood chips

Mechanical pulping is an energy intensive process. Energy requirements for a given product quality are determined by the quality of raw material (i.e. moisture content, density), the action and efficiency of pulping equipment and the pulping process (Miles and Karnis 1995). It has been shown in the literature (Sabourin 1998; Kure et al. 1999) that compressive pre-treatment prior to refining gives a reduction of refining energy by up to 20%.

Effects of compressive pre-treatment on wood and fibre morphology were first described by Frazier and Williams in 1982. In 1997, Andritz introduced a revised type of compression screw equipment called RT Impressafiner, with a short preheating time of 15 s, compression ratio (5:1) and pressurized conditions (1.5 bar) allowing higher temperature (Sabourin 1998). The first Impressafiner full scale installation was in 1999 in Bowater Calhoun Tennessee, USA, using as raw material loblolly pine with high level of extractives. In 2008, Holmen Paper Braviken mill, Sweden installed an Impressafiner in full scale. As raw material the Braviken mill is using Norway spruce which have lower level of extractives than Loblolly pine. In a thermomechanical pulp process the Impressafiner is located in the begining of the process, after chip wash, before preheater and refining, see *Figure 2.2*

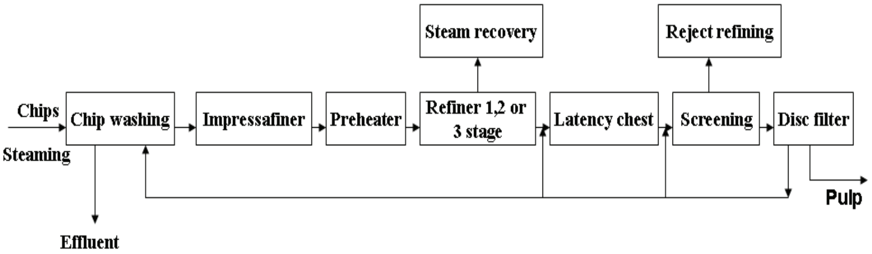

Figure 2.2: TMP line with an RT Impressafiner system.

The Impressafiner is designed to soften (preheating time 15 s, pressure 1.5 bar) and compress the chips to a uniform size distribution as they proceed to the discharge of the screw press. The compression applied to the wood chips (chips bulk density approx. 150 kg/m^3) increases along the shaft from the intlet to the discharge of the screw press. Interrupted flights are present on the discharge end of the screw to in order to increase chip destructuring. Interrupted flights do not wrap continously around the shaft, but instead have open sections between the flights. Destructuring levels are increased in the open sections (Sabourin 2003). As a consequence, the pretreated chips from an Impressafiner (chips bulk density approx. 750 kg/m^3) have a reduced size distribution and exhibit some degree of partial defibration, but the fibers are still intact (Sabourin 2000; Sabourin et al. 2002). The structural changes in the wood chips accelerate and improve the uniformity of heating, thus allowing a reduction in time required to soften the wood. *Figure 2.3* and *Figure 2.4* illustrate white spruce wood chips before and after compressive pre-treatment in a pilot Impressafiner.

Figure 2.3: White spruce wood chips before pre-treatment.

Figure 2.4: White spruce wood chips after pre-treatment in an Impressafiner (temperature 111°C, retention time 15 s, compression ratio 5:1).

Mechanical pre-treatment of wood chips prior to refining has been shown to open up the wood structure before refining, to minimize variation in moisture content, maximize the removal of extractives, reduce variation in bulk density and reduce the energy consumption during subsequent refining (Sabourin 1998; Sabourin 2000).

Moreover, the high compression ratio inside the Impressafiner, squezees out organic substances (e.g. extractives) from the wood chips before refining, thus reducing the amount of detrimental substances that enter the pulping and papermaking processes (Sabourin et al. 2002). The organic substances removed from the Impressafiner will enrich in the process water. Handling of this water is important in order to avoid that the detrimental substances enter the effluent treatment or reach undesirable levels in the process water.

2.1.3 Dissolved Air Flotation

For the pulp and paper industry water consumption is important: 5-15 m^3 of fresh water are used to produce 1t of paper in a newsprint mill (Thompson et al. 2001). Due to the environmetal regulations, paper mills have to reduce their fresh water consumption and effluent discharges to the water recipients. There are also economical incentives for reducing mill effluents as a higher degree of system closure would result in savings in terms of fresh water, energy and raw material consumption (Widsten et al. 2004). Closure of water system causes accumulation of detrimental substances, hence increases runnability problems. Unless dissolved and colloidal substances are eliminated by an in-mill treatment (i.e flotation unit, membrane filtration, oxidation, biological treatment, evaporation), they leave the paper mill either with the final product or in the process effluent (Widsten et al. 2004).

Dissolved Air Flotation (DAF) is a method used for removing particles from water using micro bubbles. The process has proved to be successful for water clarification in the paper industry. Dissolved Air Flotation is often used in the deinking process and external wastewater treatment plants. DAF has also been applied for removal of extractives from thermomechanical process waters: cloudy white water (derived primarily from the disk filter that concentrates pulp after the cleaners) and reject filtrate (derived from concentrating the fibre prior to reject refining) (Richardson and Grubb 2004), in a eucalyptus kraft mill in order to control pitch deposition (Negro et al. 2005) and for removal of detrimental substances from peroxide-bleached thermomechanical pulp water (Saarimaa et al. 2006). It was found that 80-90% of the fibre-bound and colloidal extractives could be removed in this way.

Flotation generally does not efficiently remove particles smaller than a few µm, and thus particles smaller than that have to be flocculated before flotation (Back 2000). A wide range of chemicals have been developed in order to flocculate dissolved and colloidal substances and to remove them from the system by using DAF. Common chemicals include aluminium sulfate, ferric chloride, aluminium based products such as poly-aluminium chloride (PAC), minerals such as bentonites or talcs and organic polymers such as cationic polyacrylamide (C-PAM), Poly-DADMAC, polyethylene oxide (PEO), etc.

A schematic illustration of a pilot DAF unit is shown in *Figure 2.5*. The process water samples to be treated are dosed with different concentrations of polymer, mixed and transported with a pump to the flotation cell. The air saturated water (5-6 bar) is mixed with flocculated process water and injected in the middle of the flotation cell and bubbles are released into the flotation cell. The flocculated particles attach to the bubbles, which rise to the surface, taking with them much of the undesirable components of the process water. As a consequence a layer of sludge is formed which is then removed mechanically by a skimmer. The DAF process gives a relatively clean subnatant that can be reused in the process.

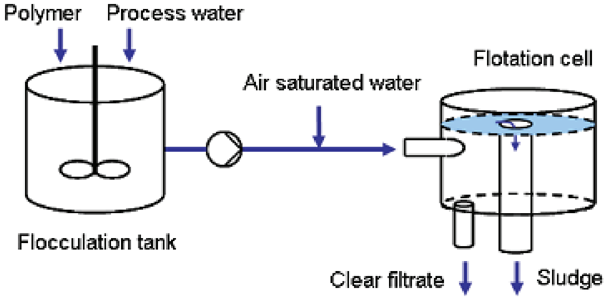

Figure 2.5: Ilustration of a Dissolved Air Flotation unit.

DAF plays an important role in the treatment of process water streams concentrated in extractives, as it efficiently removes extractives from the process water to avoid a build up in the TMP process water loops. Moreover, DAF units have been shown to efficiently remove COD and the flocculated extractives, mainly depending on the process characteristics (wood species, pH, temperature) and on the location of the DAF in the mechanical pulping process.

Floc strength

Floc strength is an important property in separation processes since break-up of flocs can affect the efficiency of the separation process. Flocs formed for removal in DAF that subsequently break-up into many smaller flocs may be captured less efficiently by air bubbles.

Floc strength is directly related to floc structure and is, therefore, highly dependent on the flocculation mechanism (i.e charge neutralization, bridging flocculation). Patch charge flocs are generally compact and their dimensions are considerably smaller than those of bridge flocs, which usually have a loose, voluminous structure. This affects retention and has important consequences for formation and drainage (Horn and Linhart 1996).

The combined processes of coagulation and flocculation aim to increase particle size for increased removal efficiency of very small particles (Jarvis et al. 2005). In a sheared suspension, flocculation may occur quite rapidly, but the flocs eventually reach a limiting size and no further flocculation occurs. This limiting size depends on the applied shear rate and on the strength of the flocs (Gregory 1988). In some cases, because of the irreversible nature of floc breakage, flocs are unable to re-grow if broken at a higher shear rate (Jarvis et al. 2005).

2.2 Dissolved and colloidal substances

During mechanical pulping processes up to 5% of the wood material are released into the process waters. This material consists of carbohydrates, low-molar mass organic acids, pectic acids, lignans, lipophilic extractives and lignin related substances (Thornton 1993). The predominant portion of the wood material is retained in the mechanical pulp fibers both after refining and subsequent bleaching. In the refining process, a yield loss of 3-5% is usually encountered with hemicelluloses being the predominant contributor (*Table 2-1*).

Table 2–1: Typical amounts of dissolved and colloidal substances in 1% suspension of unbleached spruce TMP (Holmbom 1997).

Wood component	Amount, kg/t TMP
Acetic acid	1-2
Lignans	2-3
Extractives	4-6
Hemicelluloses, pectin	18-21
Lignin	3-5
Others	6-8

However, the process conditions during alkaline peroxide bleaching affect the amount and composition of the dissolved and colloidal substances released from the fibres into the aqueous phase. As a consequence of these changes, a further yield loss of around 3% (on wood) can be found after a peroxide stage (Gellerstedt 2009).

Dissolved substances

Hemicelluloses are one of the main constituents of wood, usually between 20 and 35% of dry mass. Hemicelluloses are found in the matrix between cellulose fibrils in the cell wall. In mechanical pulping, hemicelluloses are partly dissolved from fibres into the aqueous phase. The most common hemicelluloses in softwood are o-acetyl-galactoglucomannans. During production of wood-containing paper, mannans are released into the process water. Mannans are known to increase the stability of colloidal wood extractives, by adsorbing on the surface of the colloidal extractives droplets and thereby stabilizing the colloids sterically (Sundberg K et al. 1994a). However, dissolved glucomannans are deacetylated during peroxide bleaching process; mannans without acetyl groups are less soluble, and are deposited onto the TMP fibres. This deposition leads to hydrophilisation of the fibres and improved sheet strength (Holmbom et al. 1995).

Pectins are present in the middle lamella between cells of all types. Pectins are highly charged polymers which may be dissolved into the water phase, particularly under alkaline conditions (Thornton et al. 1994). Pectic acid are known to consume cationic retention polymers in the process water and thus reduce the effect of the added polymers. Norway spruce contains 1-2% pectins (Sundberg A. et al. 1996).

Lignin is the second most abundant natural polymer next to cellulose and is one of the most complex naturally occurring high molecular weight materials. Lignin is formed by the enzymatic dehydrogenation of phenylpropane followed by radical coupling. The concentration of lignin is high in the middle lamella, but due to the thickness of the secondary wall, 70% of the lignin is found here. Lignin has a very low solubility in most solvents which makes studying of the macromolecule difficult (Andersson 2010).

Lignans are characterized by two phenylpropane units bound together at their β-carbon, hydroxymatairesinol is the most abundant lignans in wood and effluents. The lignans are released from the wood structure during chip washing and impregnation in the pulping process. Very small amounts were released in the later pulping stages (Jørgensen et al. 1995). Lignans can be extracted by methyl tert-butyl ether (MTBE) and therefore are considered as extractives. However, lignans comprise a component group of their own, in many aspects they are considerably different from the lignin material and the extractives.

Colloidal substances - wood extractives

Norway spruce (*Picea abies*), the main species used for mechanical pulp in Europe, contains about 1% lipophilic extractives that are composed mainly of fatty acids, resin acids, sterols, steryl esters and triglycerides (Sjöström 1993).

The resin acids can be divided into two groups: the primarane-type and the abietane-type. The primarane type of resin acids has methyl and vinyl groups at the C-13 position, see *Figure 2.6*. The abietane type has an isopropyl or isoprenyl group at this position and their double bonds are conjugated. A special resin acid is dehydroabietic acid, having an aromatic ring (Ström 2000). The resin acids are the compounds causing the main part of the toxicity in effluents from mechanical pulping.

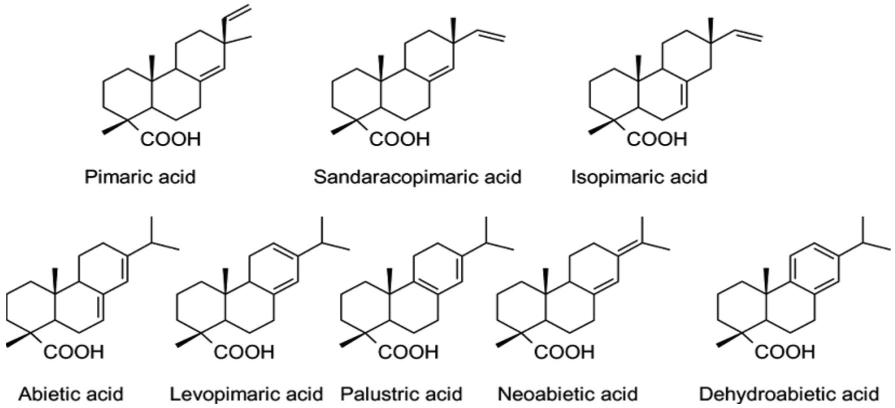

Figure 2.6: Chemical structure of the main resin acids.

The dominating fatty acids in most wood species are straight chain saturated or unsaturated fatty acids with 16-24 carbon atoms. The mono-, di- and triunsaturated acids with 18 carbon atoms dominate in most softwood species, see *Figure 2.7*. The fatty and resin acids dissociate at sufficiently high pH and can dissolve in alkaline water depending mainly on temperature and metal ion concentration (Ström 2000).

The steryl esters and triglycerides are esters of sterols and glycerol with fatty acids. These componds are hydrophobic and have low solubility in water (Ström 2000).

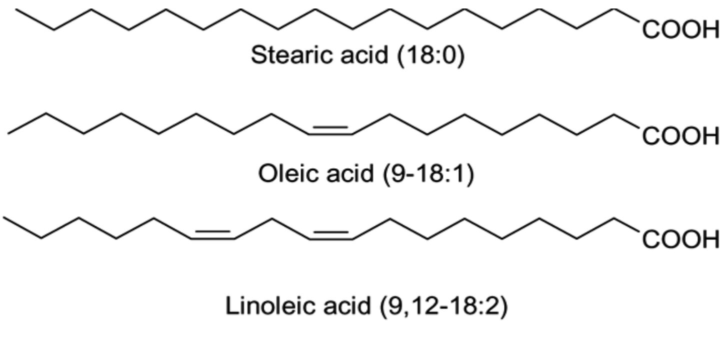

Figure 2.7: Chemical structure of the main fatty acids.

Wood extractives may be dissolved in the process water, attached to fines and fibres or exist as suspended colloids in the size range of 0.1-1 µm (Nylund et al.1993; Swerin et al. 1993), see *Figure 2.8*.

A proper understanding of the colloidal stability, i.e. the factors controlling the tendency of these colloidal particles to agglomerate or remain suspended, is of great importance for the control of whether or not the extractives present may deposit to form troublesome pitch deposits and of how they can be separated from the process water.

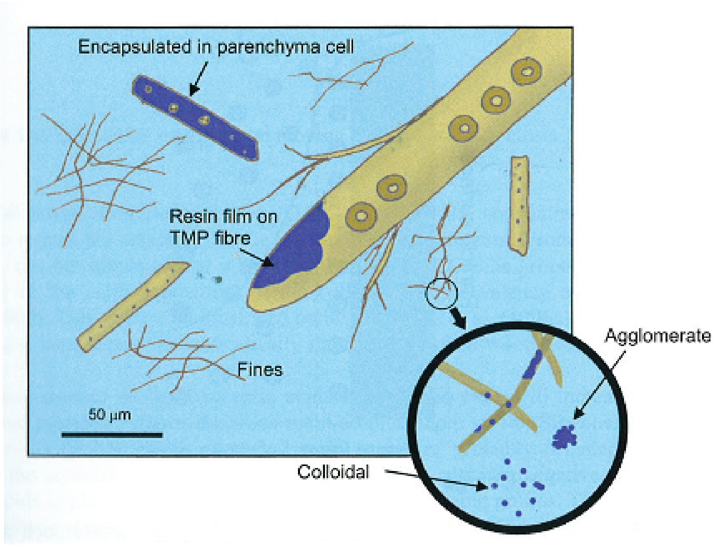

Figure 2.8: Illustration of the different physical forms of wood extractives (Johnsen 2007).

Location in wood

In wood, extractives are located mainly in resin canals, parenchyma cells (i.e. axial and ray parenchyma) and associated epithelial cells. Resin canals (*Figure 2.9*) are formed as interspaces between the fibres both vertically and horizontally in most pulpwood species. Resin canals are most frequent in pine, but are also present in spruce and other softwood species. The function of the canals is to protect the tree from invanding organism such as insects or fungi (Jansson and Nilvebrant 2009).

In softwood, usually less than 10% of the wood volume is made up of parenchyma cells, more than 95% of which occur within the rays, see *Figure 2.10*. Parenchyma cells are short and have simple thin-walled pits to traheids, to vessels, and to each other. Parenchyma resin functions mainly as food storage and is rich in fats, waxes and sterols (Back 2000).

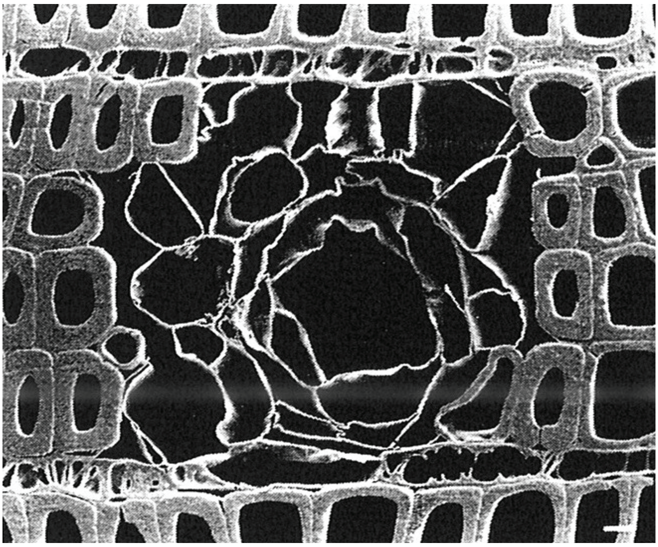

Figure 2.9: Cross-section of lodgeopole pine wood showing a resin canal. Scale bar 10 μm (Cineros and Drummond 1995).

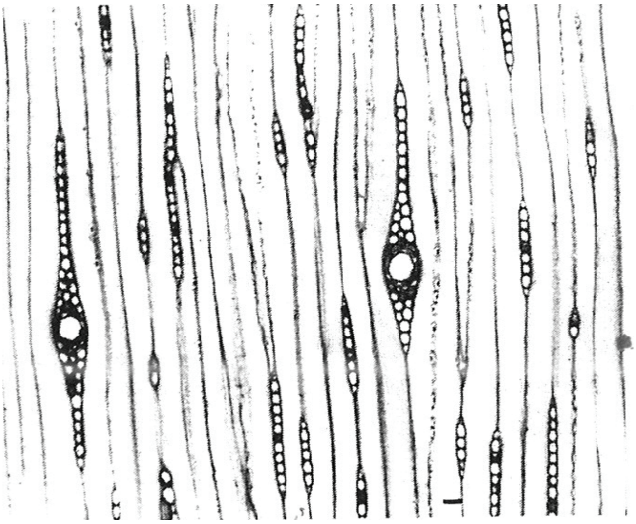

Figure 2.10: Tangential section of a softwood which reveals the rays in cross-section. Scale bar 20 μm (Cisneros and Drummond 1995).

There are fundamental differences between extractives localized in resin canals and parenchyma cells, and between the different wood species (i.e. pine, spruce), both with regard to physical accessibility and chemical composition (Back 2000). Fernando et al. (2008) found that pine chips contained three to five times more extractives than spruce chips. Moreover, 70% of the extractives in pine are located in the resin canals, while in spruce only about 45% of the extractives are located in resin canals (Back and Carlson, 1955), see *Table 2-2*. In pine, the pressure in the resin canals is high (7-12 bars), while in spruce the pressure in resin canals is high only in the young part of the sapwood (i.e. the outer 3-5 annual rings) (Engström and Back 1959). Moreover, the average pit wall area is higher in pine than in spruce. The pit size and distribution in the wood affects the dereseination rate in mechanical pulping process (Back 2000).

Table 2–2: Location of extractives in pine and spruce wood (Back and Carlson, 1955).

Wood species	Extractives in resin canals, %	Extractives in parenchyma cells, %	Average of pit wall area, %
Pine	70	30	50
Spruce	45	55	5

During primary refining in the TMP process, the integrated native wood cell structure is destroyed, allowing release of extractives from both the resin canals and those encapsulated in parenchyma cells (Cineros and Drummond 1995). However, it is considered that extractives localized in resin canals are more easily accessible, since canal resin is not enclosed within cell walls. Because it contains mainly free acids it is most easily saponified, dispersed and dissolved in alkali (Back 2000).

Furthermore, Cisneros and Drummond (1995) found that using a plug screw with high compression ratio (5:1) the resin canals are crushed and release extractives whereas parenchyma cells to a large degree survive the compression (*Figure 2.11*). They suggested that an interstage washing step should effectively reduce the amount of extractives that enter in the subsequent refining process.

In actual mill practice, the amount and composition of the dissolved and colloidal substances in process waters is dependent on many process factors, such as quality of wood species, pulping process conditions, possible washing of the pulp and the water system configuration of the mill, and especially the degree of water system closure (Mosbye 2003).

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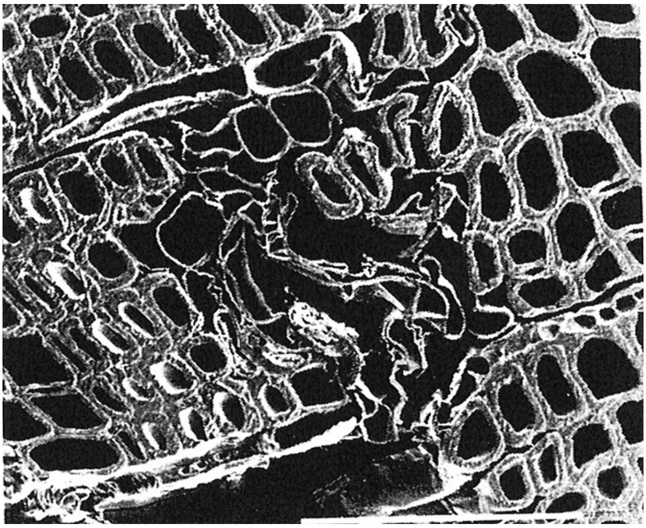

Figure 2.11: Cross-section of a lodgepole pine chips after fracturing in a crew feeder at a 3:1 compression ratio. Scale bar 100 µm (Cisneros and Drummond 1995).

2.2.1 Factors affecting colloidal stability

Colloidal stability is due to a balance of attractive and repulsive interactions at interfaces. Attraction will lead to particle growth at a rate which depends on the particle concentration (i.e. frequency of particle collisions due to diffusion), hydrodynamic conditions and range of the attractive interactions. Eventually, attachment of particles to each other leads to formation of large aggregates that may separate and, e.g., form deposits. Deposits may obviously also be formed by direct attraction of colloidal particles to solid surfaces (machine equipment, fibers).

The surface interactions that influence colloidal stability are those due to Van der Waals forces, diffuse ion layers at charged surfaces and adsorbed or dissolved polymers. Other important but theoretically less well clarified interactions are effects of solvation and hydrophobic interactions (Stenius 2000). The main factors that affect the colloidal stability of extractives are particle concentration, pH, electrolyte concentration, temperature, viscosity, chemical composition of the extractives (Allen 1979; Blanco et al. 2005) and the presence of adsorbing wood polymers or polymeric additives.

2.2.2 Electrostatic stabilization

Under papermaking conditions the dissolved and colloidal substances are negatively charged, predominantly due to the dissociation of carboxylic groups in fatty acids, resin acids and hemicelluloses (Sundberg A. et al. 2000). Dissociation of fatty and resin acids in the surfaces of extractive particles leads to the formation of a diffuse layer of small ions from the surrounding electrolyte solution outside the particle surface. When two particles collide, the diffuse layers repel each other, thus preventing particles from attaching to each other. Diffuse layers are compressed when the electrolyte concentration increases and for the repulsion to be sufficiently strong, the concentration should be below 0.1 M of 1:1-electrolyte and below 0.01 M of 2:1 electrolyte, where the divalent ion is a cation (Hiemenz and Rajagopalan 1997; Stenius 2000).

An increased amount of fatty and resin acids will increase the surface charge density of the colloidal wood resin resulting in increased stability of the colloidal droplets (Sihvonen et al. 1998). However, increased protonation of the carboxylate ion of fatty and resin acids at pH below 4 decreases the surface charge of the colloids. Then the colloidal wood resin is no longer electrostatically stabilized and aggregates (Johnsen et al. 2004).

Thus, electrostatically stabilized colloidal wood extractives, can be destabilized at relatively low electrolyte concentrations. Another way of destabilization is based on the use of cationic polyelectrolytes that neutralize the surface charge by adsorption. On the other hand, adsorption of excess polyelectrolyte may lead to restabilization (Stenius 2000).

2.2.3 Steric stabilization

Another technically important stabilization mechanism of colloidal dispersions is steric, or polymer stabilization (Shaw 1980; Eklund and Lindström 1991). This is due to the adsorption of soluble polymers on the particle surface. Such layers repel each other when particles collide. This type of repulsion is effective even at very high salt concentrations.

Pure dispersions prepared from the colloidal wood extractives are electrostatically stabilized (Sundberg K. 1995). However, particles in dissolved and colloidal substances from TMP often do not agglomerate even at high salt concentrations. This stability against salt is due to steric stabilization. Dissolved hemicelluloses, mainly mannans, accumulate around droplets, thus preventing them from aggregating.

The adsorption of hemicelluloses on extractive colloids and their stabilizing effect on colloidal wood resin has been studied extensively (Johnsen et al. 2004, Sihvonen et al. 1998, Sundberg et al.1994a, Sundberg et al 1994b). The steric stabilization of colloidal resin is due to adsorption of dissolved hemicelluloses, especially galactoglucomannans (Pelton et al. 1980; Hannuksela et al. 2004; Sundberg A. et al. 1996; Allen 1979; Swerin et al. 1993; Holmbom and Sundberg 2003) and prevents the colloids from aggregating at the addition of salt even when the electrostatic forces become insignificant. The stability of resin reduces its ability to form deposits (Otero et al. 2000).

2.2.4 Polymer - induced flocculation

In papermaking, polymers are often added to the process in order to increase the retention of small particles like fillers and fines (i.e. retention aids) or to adsorb, or fix, dissolved and colloidal substances to the fibre web (i.e. fixatives). Such additives are also known as process aids since they are used to improve the production efficiency (Mosbye 2003).

Flocculation of colloidal particles by adsorption of polymers is an important phenomenon in papermaking, water treatment, dissolved air flotation and, in general, in processes were it is desired to rapidly remove as much as possible of the colloidal particles from a suspension (Stenius 2000). Both the retention and flocculation behaviour of the system will depend on the molecular interactions between the components. Many of the components are charged and thus the valency and the concentration of electrolyte in the solution as well as the solution pH will affect the interactions (Österberg 2000).

The different flocculation mechanisms are determined by the properties of the polymers used i.e. charge density and molecular mass. High charge and low molecular mass polymers induce flocculation by charge neutralization mechanism while low charge and high molecular mass polymers are able to bind particles from a larger distance than high charge, inducing bridging flocculation (Swerin et al. 1997).

Charge neutralization ("patch flocculation") mechanism

A high charge density and low molecular mass polymer adsorbs on particle surfaces in a flat conformation. Flocculation occurred as the result of attractive forces between oppositely charged patches of colliding particles (Horn and Linhart 1996) (*Figure 2.12*).

Patch-charge flocs are generally compact and their dimensions are considerably smaller than those of bridge flocs. Moreover, the flocs are sensitive to polymer dose and break easily due to shear forces. They may not be formed at all if the shear forces are very strong because attraction is too short-range to overcome repulsive hydrodynamic interactions. If the polymer is added in excess over the amount required to neutralize particle charge, restabilization can occur. This may be due to steric stabilization or charge reversal (Stenius 2000).

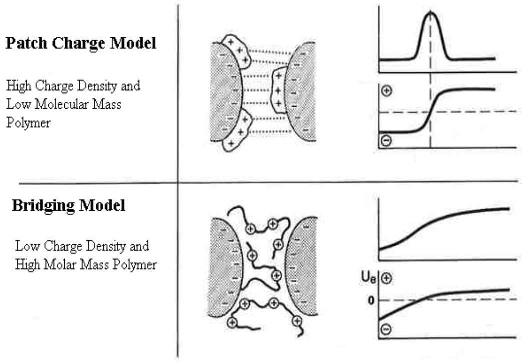

Figure 2.12: Schematic drawing of patch charge and bridging flocculation mechanism (Horn and Linhart, 1996).

Bridging flocculation mechanism

Polymers that adsorb loosely to surfaces so that they form long dangling ends and loops may give rise to flocculation by bridging (*Figure 2.12*). This involves interactions of the dangling ends of the polymer with other particles so that loose flocs are formed. Polymer bridging produces voluminous flocs which may easily be broken down by shear forces (Stenius 2000). The efficiency of polymer bridging is closely connected with the solvency of the medium and the molecular weight of the polymer. High molecular weight permits easier formation of bigger aggregates whereas a good solvent ensures a maximum of extension for the loops and tails in the solution (Lafuma 1996). These loops or tails may adsorb to other particles, creating a bridge, and the result is large flocs which are retained in the fibre web (Mosbye 2003).

2.3 Handling of wood extractives in the process water

Washing mechanical pulp is a good way to remove extractives (Käyhkö 2002), but the efforts to close water circuits imply that washing mechanical pulp require fibre recovery and hence, becomes less efficient. Thus, in order to achieve high closure, it becomes necessary to eliminate harmful substances or at least to decrease their negative effect as early as possible in the process. Using equipment for compressive pre-treatment of the chips, such as an Impressafiner, it was shown that the chips have some degree of partial defibration but the fibres are still intact (Sabourin 2000; Sabourin et al. 2002). Moreover, extractives can be removed from the wood chips before refining, thus reducing the amount of extractives that enter the pulping and papermaking processes (Sabourin et al. 2002; Tanase et al. 2010). The extractives removed from the Impressafiner will enrich in the process water. Handling of this water is important in order to avoid that the extractives enter the effluent treatment or reach undesirable levels in the process water.

Methods used to prevent detrimental substances from circulating in the white water system and reduce deposition problems are attachment to the pulp fiber with chemicals (retention aids, e.g. organic polymers) or adsorption onto special pigments (Wågberg and Ödberg 1991; Sundberg A. et al. 1993). Apart from binding them in to the paper web, dissolved and colloidal substances can be removed from the process water by sedimentation, filtration, flotation, reverse osmosis, etc. The choice of the cleaning technique depends on which process stage that is best suited for deresination of the wood fibre and concentration of extractives in the specific process water among other factors.

CHAPTER

3

MATERIALS AND METHODS

3.1 RT Impressafiner

The Impressafiner (*Figure 3.1*) is designed to compress the chips to a uniform size distribution as they proceed to the discharge of the compression screw press. Simultaneously the Impressafiner squezees out extractives and dissolved organic substances. The high compression level in the Impressafiner, in addition to inducing maceration of the wood chips also results in the production of some broken fibres and fines. For more details, see **Paper I.**

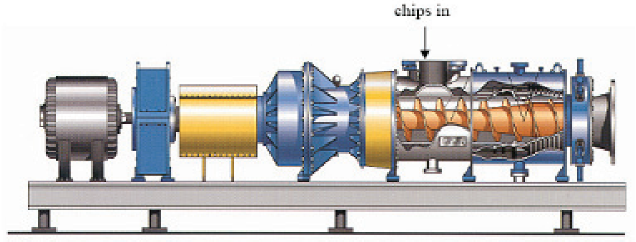

Figure 3.1: Andritz MSD 500 Impressafiner.

3.1.1 Impressafiner - Pilot scale trails

Raw material

Freshly cut loblolly pine (*Pinus Taeda*) chips were obtained from South Carolina (USA) and white spruce (*Picea Glauca*) was obtained from a forest in the Wisconsin (USA).

Operating conditions

The Impressafiner operating conditions in pilot scale were: temperature 125^{o}C, retention time 15 s, pressure 1.4 bar, compression ratio 5:1 (increase from the inlet to the discharge of the screw press). The production rate in the pilot scale Impressafiner was 18 - 19 t/d. The Specific Energy Consumption (SEC) was about 40 kWh/t.

3.1.2 Impressafiner - Mill scale trials

Raw material

Norway spruce (*Picea Abies*) chips were used in Holmen Paper Braviken mill, Sweden.

Operating conditions

The Impressafiner operating conditions were: temperature 111^{o}C, retention time 15 s, pressure 0.5 bar, compression ratio 5:1 (increase from the inlet to the discharge of the screw press). The Specific Energy Consumption (SEC) in mill scale Impressafiner was 20 kWh/t, having a production rate of 30 t/h.

Both pre-treated chips and pressate liquors were collected and they were analyzed for the amount and composition of extractives. For more details see **Paper I.**

3.2 Dissolved Air Flotation

3.2.1 Dissolved air flotation - laboratory trials

Raw material

Two different mill process water samples were used in our study. One from the equipment used for pre-compression of chips from Norway spruce (Andritz 500 MSD Impressafiner) in the TMP B line, at Holmen Paper Braviken mill, Sweden and one from a chip washer, at Norske Skog Skogn mill, Norway. The water samples from the Impressafiner were transported to the laboratory at NTNU where they were stored in a frozen state until required for testing and treatment. The process water samples from the chip washer were used fresh, without freezing.

Chemicals

Solutions of Poly-(N-N-dimethyldiallyl-3-4-ethylene-pyrrolidonium)chloride, Poly-DADMAC, i.e. a polymer with high charge density (CD) and low molecular mass (Mw) and a cationically modified polyacrylamide, poly(trimethyl(3-methacrylamidopropyl)-ammonium)chloride, C PAM, i.e. a polymer with high Mw and low CD (Kemira Oyj, Finland), were used (Table 3-1). They were used as delivered without further purification.

Table 3–1: Properties of the cationic polymers used. *DS* is the degree of substitution, i.e. the fraction of monomers in the polymer that carries a cationic group.

Substance	M_w 10^6 g/mol	CD meq/g	DS mol-%
Poly-DADMAC	0.17	6.2	100
C-PAM	7.0	0.3	2.0

Dissolved air flotation experiments

The flotation experiments were performed using a laboratory scale DAF (*Figure 3.2*) unit at room temperature and at the native pH of the process water (pH 5.5). The volume of the sample in the cell was 1000 ml and the height of the column of process water was 41 cm. Various amounts of flocculation chemicals were added to the process water during slow agitation (1 min, 100 rpm) in order to promote the interaction of the flocculants with dispersed organic substances and to facilitate the growth of the flocs.

Air-saturated water (5 bar, 23°C) was injected at the bottom of the flotation cell. A constant time, 7 min was allowed to pass after addition of flocculants before the air-water mixture was released into the flotation cell. Flocs formed by the polymers and extractives attached to the bubbles and rose up to the surface. After 10 min, a sample of the subnatant was taken and subjected to analysis of turbidity, chemical oxygen demand (COD) and lignin content as well as content and composition of carbohydrates and extractives. More details are given in **Paper III**.

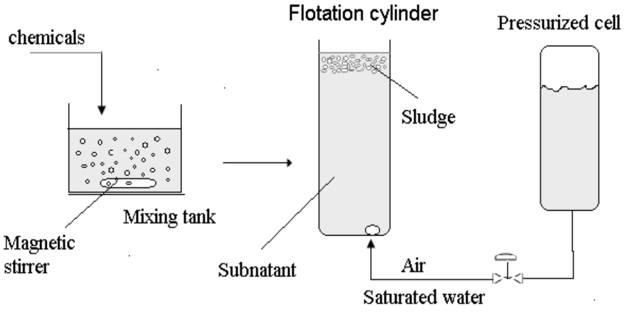

Figure 3.2: Scheme of the laboratory dissolved air flotation unit.

3.2.2 Dissolved air flotation - pilot trial

Raw material

The water samples were collected from the equipment used for pre-compression of chips from Norway spruce (Andritz 500 MSD Impressafiner) in the TMP B line at Holmen Paper Braviken mill, Sweden. In order to simulate real DAF process conditions, the Impressafiner pressate water samples were collected and used directly in the pilot dissolved air flotation trial at the mill side. The chemicals used in dissolved air flotation pilot trial were the same chemicals used in laboratory tests.

Dissolved air flotation experiments

Dissolved air flotation tests were performed in a pilot flotation unit (*Figure 3.3*) at the Holmen Paper Braviken mill. The experiments were performed at 70^{o}C and at pH 6.6-7.1. The volume of the sample in the DAF cell was 10 l. Various amounts of flocculation chemicals were mixed with Impressafiner process water in order to promote the interaction of the flocculants with dispersed organic substances and to facilitate the growth of flocs.

Air-saturated water (temperature 70oC, pH 7.1) was mixed with flocculated Impressafiner pressate water and injected in the middle of the flotation cell in a continuous flow, 2 L/min (1/3 is pressurised water and 2/3 is mixture of Impressafiner pressate water and chemicals). The pressure used in our experiments was 6 bar. Flocs formed by the polymers and extractives attached to the bubbles and rose up to the surface. The subnatant was subjected to analysis of turbidity, chemical oxygen demand (COD) and lignin as well as content of carbohydrates and extractives. More details are given in **Paper IV.**

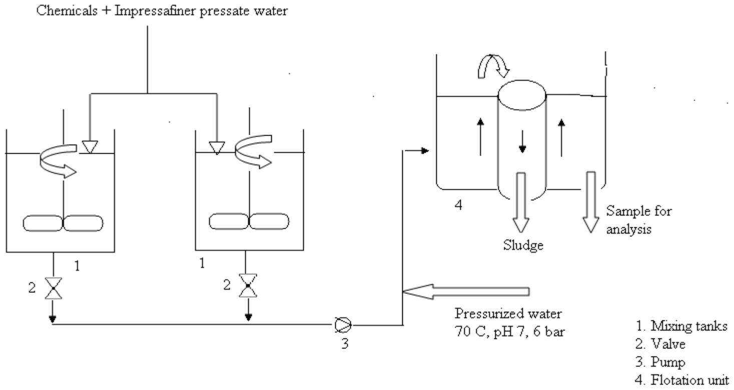

Figure 3.3: Scheme of the pilot dissolved air flotation unit.

3.3 Chemical analysis

Turbidity was measured in Nephelometric Turbidity Units (NTU), using a laboratory turbidimeter (Hach Model 2100AN). It has been shown in the literature that the concentration of lipophilic extractives correlates well with the turbidity of a colloidal substance sample when no fillers or fines are present in the sample (Örså and Holmbom 1994; Sundberg et al. 1994 and 1996; Sundberg 1995; Sundberg et al. 1993; Johnsen 2007). A sample of TMP process water generally is turbid due to the light scattered by the colloidal substances. The scattering mainly comes from particles formed by insoluble extractives released from the pulp. More details are given in **Paper I.**

The *Chemical Oxygen Demand*, COD, was measured according to the Dr. Lange method (ISO 6060-1989).

The residual *lignin* was determined by extracting the lignans from the process water with methyl tert-butyl ether (MTBE) (Örså and Holmbom 1994) and measuring the absorbance at 280 nm using a UV-Vis spectrophotometer.

The amount of *carbohydrates* was determined using the methods described by Chaplin and Kennedy (1986). The process water from both Impressafiner and Chip washer (1 ml) was mixed with 1 ml phenol solution (5 g /100 ml) and 5 ml concentrated sulphuric acid (96%). Thereafter, it was allowed to cool down for 10 minutes, mixed well and left for cooling for 30 minutes. The total amount of carbohydrates (see Table 2) is determined by measuring the light absorbance at 490 nm.

The amount and composition of *extractives* in the process water was analyzed as soon as possible after sampling by extraction with methyl tert-butyl ether (MTBE), using the method described by Örså and Holmbom (1994).

Particle size distribution was performed with a Malvern Mastersizer (Malvern Instruments Ltd, UK). More details are given in **Paper II**.

Electrophoretic mobility of the water suspensions was determined at different levels of addition of cationic polymers in order to determine the surface-charge characteristics. Knowledge of particle charge or surface potential is essential to control the stability and coagulation of colloidal systems (Stenius 2000). Measurements were performed using a Malvern Zetasizer Nano ZS instrument (Malvern Instruments, UK) at different concentrations of polymers. More details are given in **Paper II.**

Sedimentation rate was measured with a Turbiscan Lab instrument (FormulAction, L'Union, France). Turbiscan is an optical instrument used to detect physical destabilizations of a water suspension. Two major destabilization phenomena affecting the colloidal stability of a water suspension are particle migration (creaming, sedimentation) and particle size variation or aggregation (coalescence, flocculation). The principle of this instrument is shown in *figure 3.4.* A detection head with two synchronous detector heads scans the entire length of the sample in a flat-bottomed cylindrical cell, acquiring transmission and backscattering data. The stability or instability of the sample is determined by analyzing the time graph. For details, see **Paper II**.

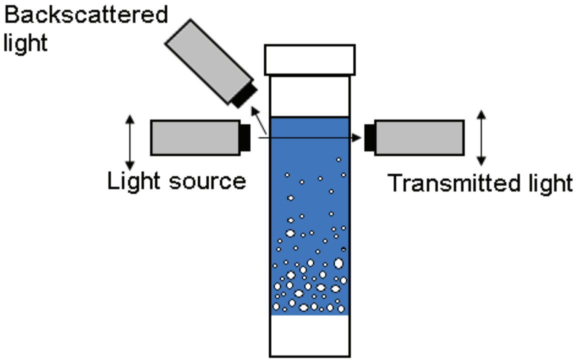

Figure 3.4: Schematic drawing of the Turbiscan mechanism principle

CHAPTER

4

SUMMARY OF PAPERS

4.1 Mass balance of lipophilic extractives around an Impressafiner in mill and pilot scale (Paper I)

The objective of the study reported in this paper was to investigate the possibility to remove extractives from the wood chips of different raw materials before refining, using a compressive pre-treatment (i.e. Impressafiner), thus reducing the amount of extractives that enter the pulping and papermaking process, without loss of fibres. In some cases the total energy consumption during subsequent refining can also be reduced.

A mass balance of extractives around a mill scale Impressafiner installation was also determined. The amount and composition of extractives released to the pressate water was related to the production of chips through the Impressafiner.

The colloidal stability of extractives present in the pressate water from Impressafiner and their flocculation behaviour by cationic polymers was also investigated. A more detailed study of the flocculation behaviour of extractives present in the pressate water from an Impressafiner using cationic polymers is presented in **Paper II**.

4.1.1 Pilot scale vs mill scale trial Impressafiner

Two raw materials were used in the pilot scale trial: loblolly pine and white spruce and in the mill scale trial the raw material used was Norway spruce. The results from both pilot and mill scale trials (*Table 4-1*) showed that by using an Impressafiner it was possible to reduce the total amount of extractives that enters in the first stage refiner.

The results from both, pilot and mill scale Impressafiner show that it was mainly resin acids that could be removed (see *Table 4-1*) while fatty acids to a large degree remained in the chips. The amount of sterols was not reduced in pilot scale while in the mill scale 10% of sterols were reduced. The results also show that up to 40% of the extractives were removed from pine which is more than from spruce chips (15% of extractives were removed) by using an Impressafiner. This is because of the difference in the extractives composition and the morphological difference between pine and spruce. Back and Carlson (1955) have found that extractives in pine are up to 70% located in resin canals, while in spruce only about 45% of the extractives are located in resin canals. Moreover, Cisneros and Drummond (1995) found that extractives in resin canals are easy accessible in chips and can be dispersed or dissolved during compression, while extractives in parenchyma cells are not easy accessible.

Table 4–1: Removal of extractives from chips through Impressafiner and pilot and mill scale.

Raw material	Total fatty acids %	Resin acids %	Sterols %	Total removal of extractives , %
Loblolly pine	8	65	-	40
White spruce	4	38	-	10
Norway spruce	14	35	10	15

4.1.2 Mass balance of extractives around Impressafiner in mill scale

For a spruce TMP mill with a capacity of 700 t/day, a mass balance of extractives was calculated from the flows around the Impressafiner and revealed that 7 t/day of extractives will enter the mill and 15% of the extractives (~ 1 t/day) will be enriched in the process water. Moreover, the results from the composition of the pressate water from the Impressafiner indicates that it was mainly resin acids (35%) that could be removed while the fatty acids (7%), steryl esters (10%) and triglycerides (7%) to a large degree remained in the chips. This is because during chip compression resin canals are crushed and release extractives whereas parenchyma cells largely remain intact and retain extractives.

SEM images of loblloly pine chips taken before (*Figure 4.1*) and after (*Figure 4.2*) the Impressafiner yielded additional information on how the compression ratio affect the liberation of extractives from chips.

Our results are in agreement with what Cisneros and Drummond (1995) found for lodgepole pine that has passed a screw feeder with a compression ratio of 5:1. They found that more than 70% of the parenchyma cells in pine retained their extractives; while more than 90% of the parenchyma cells were damaged after 1st stage refining. Thus, extractives both from resin canals and parenchyma cells were liberated after the primary refining stage, but there may have been a preferential liberation from resin canals during chip compression.

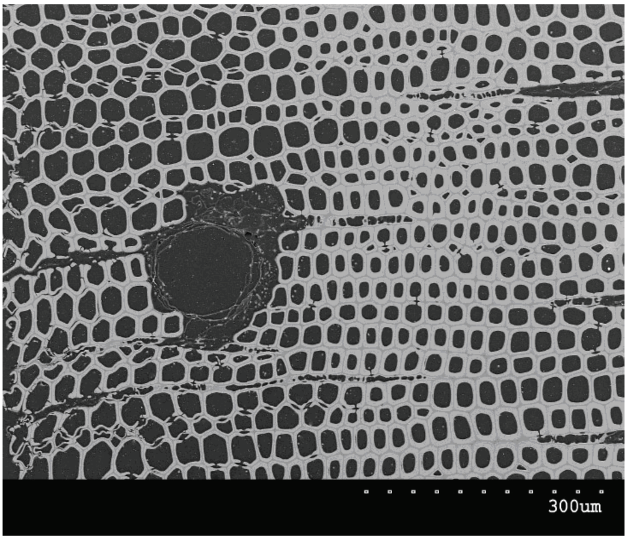

Figure 4.1: SEM image of a loblolly pine chip containing a resin canal before Impressafiner.

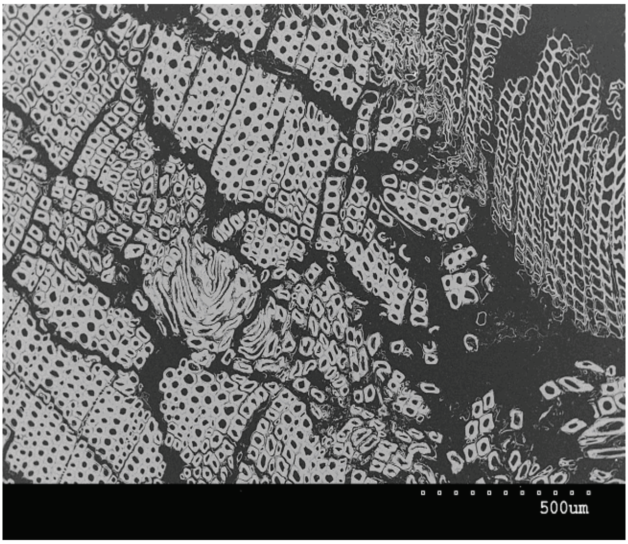

Figure 4.2: SEM image of loblolly pine chips after Impressafiner (temperature 125^{o}C, retention time 15 s, compression ratio 5:1).

4.1.3 Stability of wood extractives

The stability of dispersed wood extractives against salt induced aggregation can be evaluated by simple turbidity measurements. The results show that the lipophilic extractives pressent in Impressafiner pressate water samples remained relatively stable in the presence of electrolytes; little aggregation resulting in sedimentation by centrifugation occured (*Figure 4.3*).

Our results are in agreement with previous results from the literature suggesting that the colloidal extractives present in the process water from unbleached thermomechanical pulp are sterically stabilized by dissolved polymers, originating mainly from wood (Allen 1979; Swerin et al. 1993; Sundberg 1995). Hence, in order to aggregate the sterically stabilized colloidal extractives effectively in process waters, either organic or inorganic fixation aids are needed (Sundberg et al. 1994).

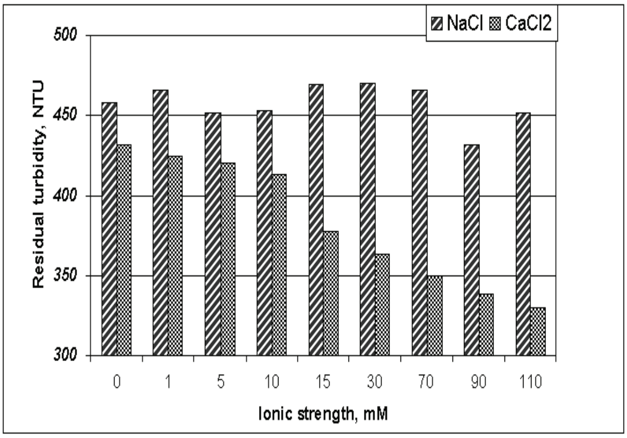

Figure 4.3: Residual turbidity after addition of salt to pressate water from Impressafiner.

4.2 Flocculation of colloidal wood extractives in process water from precompression of chips in thermomechanical pulping (PaperII)

The aim of this work presented in **Paper II** was to obtain a better understanding of the effects of two different cationic polymers on the interactions with colloidal extractives in the pressate water from an Impressafiner. A high charge density and low molecular mass polymer (poly-DADMAC) and a high molecular mass and low charge density polymer (C-PAM) were used in our study. Moreover, the combination of the polymers (poly-DADMAC + C-PAM, mass ratio 1:1) were also used in our study. The goal of this study was to clarify in which way the properties of the polymers affect the mechanism behind flocculation and floc strength.

4.2.1 Effect of cationic polymers on interaction with dissolved and colloidal substances

Adding cationic polyelectrolytes to a suspension may introduce attractive forces, such as bridging, or reduce electrostatic repulsion by neutralizing the particle surface charge, see *Figure 4.4*. In both cases, polyelectrolytes act as flocculants. They can also act as stabilizers, if their adsorption changes the forces between the surfaces to repulsive, such as steric repulsion or electrostatic repulsion due to charge reversal (*Figure 4.5*). Thus, the role of polyelectrolyte is a matter of dosage (Stenius 2000).

It is generally assumed that high molecular mass and low charge density polymers induce bridging flocculation, while high charge density and low molecular mass polymer flocculate by charge neutralization (Swerin et al. 1997; Stenius 2000).

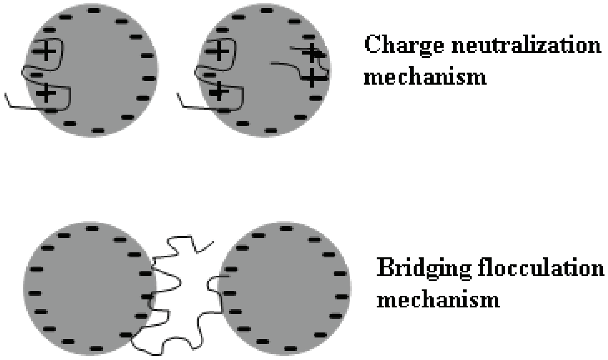

Figure 4.4: Schematic illustration of chrage neutralization and bridging flocculation mechanism.

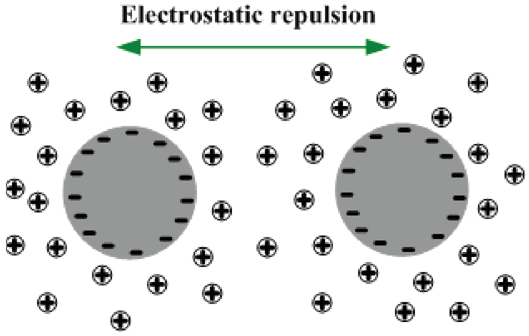

Figure 4.5: Ilustration of the electrostatic repulsion mechanism.

Electrophoretic mobility of the water suspensions was determined at different levels of addition of cationic polymers in order to determine the surface-charge characteristics, see *Figure 4.6*. Knowledge of particle charge or surface potential is essential to control the stability and coagulation of colloidal systems (Stenius 2000).

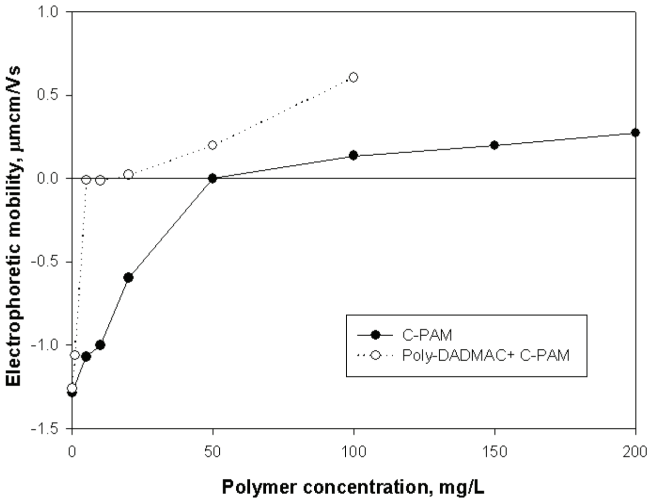

Figure 4.6: Electrophoretic mobility measured after addition of C-PAM and combination of the polymers to the Impressafiner pressate water.

The flocculation of colloidal extractives with cationic polymers was first determined by simple turbidity measurements, see *Figure 4.7*. It has been shown in the literature that the concentration of lipophilic extractives correlates well with the turbidity of a colloidal wood resin suspension when no fillers or fines are present in the sample (Sundberg A. et al. 1993; Örså and Holmbom 1994; Sundberg K 1995; Mosbye 2003; Johnsen 2007).

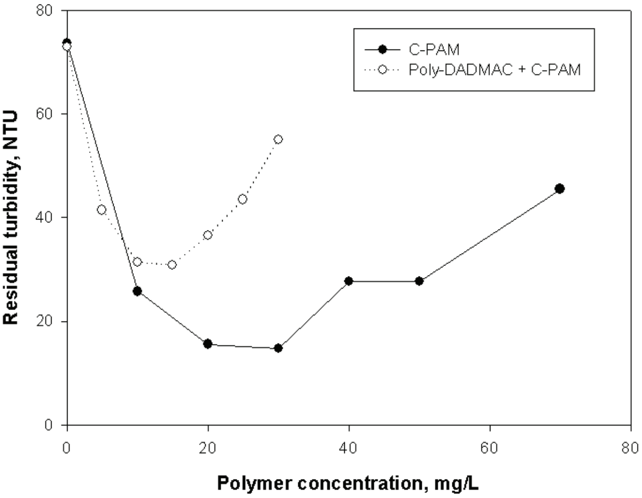

Figure 4.7: Residual turbidity measured after addition of C-PAM and combination of the polymers to the Impressafiner pressate water.

The results from electrophoretic mobility and turbidity measurements (*Figure 4.6* and *Figure 4.7*) showed that by using different cationic polymers (C-PAM or combination of polymers) it was possible to flocculate the colloidal wood extractives present in the pressate water from Impressafiner. The minimum shown in *Figure 4.7* is sometimes called the optimum polymer dose (OPD) (Sundberg A. et al. 1993) which is the polymer dose needed to obtain maximum removal of colloidal extractives. The residual turbidity increased by increasing the polymer concentration after OPD which indicated that excess of polymers may lead to stabilization rather than flocculation. Our results are in agreement with previous results from the literature (Mosbye 2003).

Sedimentation rate

The sedimentation and flocculation efficiency of the colloidal wood extractives present in pressate water from Impressafiner was also measured with Turbiscan Lab instrument. Particle migration leading to sedimentation or creaming phenomena can be characterized by calculation of the migration velocity (*Figure 4.9*), or of the sediment / cream phase thickness (deltaH) (*Figure 4.8*). The migration velocity is the slope of the clarification phase thickness (migration of the particles in the top of the test tubes over time) as a function of time. The phase thickness is the thickness of the sediment or cream layer in the test tubes. More details are given in **Paper II**.

The results are in agreement with regard to flocculation of colloidal wood extractives drawn from the turbidity measurements results.

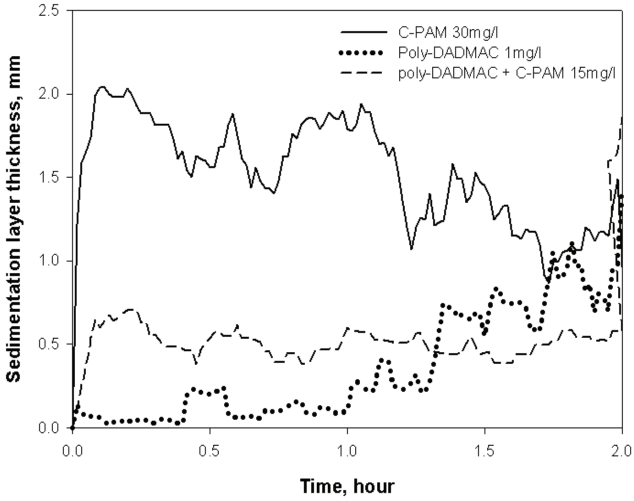

Figure 4.8: Phase thickness of sediment layer measured with a Turbiscan instrument for Impressafiner water after addition of polymers.

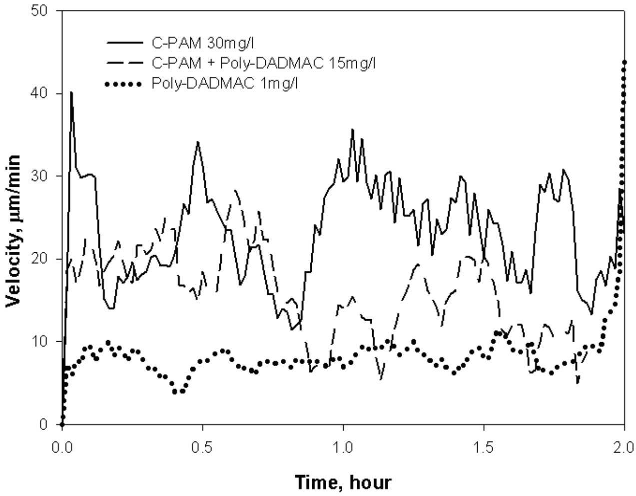

Figure 4.9: Migration velocity measured with Turbiscan instrument for Impressafiner pressate water after addition of polymers.

Particle size distribution

Particle size distribution measurements of the pressate water from the Impressafiner after addition of polymers yielded additional information on the way the polymers flocculated the colloidal extractives, see *Figure 4.10.*

C-PAM (20 mg/l) formed the largest aggregates. Combination of the polymers, poly-DADMAC+C-PAM, (mass ratio 1:1, polymer concentration 20 mg/l) induced formation of relatively large flocs, but much smaller than C-PAM alone. On the other hand, when poly-DADMAC (1 mg/l) was added the flocs formed were small and more compact. The results are in full agreement with the conclusions with regard to flocculation mechanism drawn from the Turbiscan results.

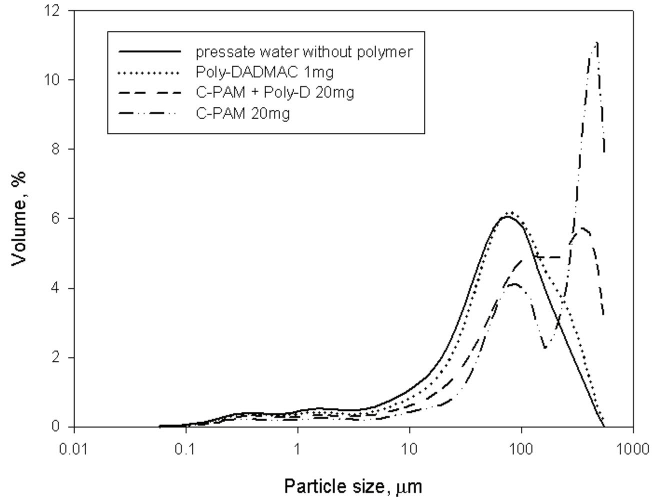

Figure 4.10: The size distribution of colloidal particles formed by extractives in pressate water from Impressafiner.

4.3 Removal of dissolved and colloidal substances from TMP process water using dissolved air flotation. Laboratory tests (Paper III)

The results from the work presented in **Paper I** and **Paper II** showed that by using an Impressafiner it is possible to remove extractives from the wood chips before the refining process and that the colloidal extractives can be efficiently flocculated by different cationic polymers. The results suggest that a flotation technique e.g. Dissolved Air Flotation (DAF) may be a convenient method to remove flocculated extractives from the process water streams.

Paper III reports on an evaluation of the removal of flocculated extractives from two thermomechanical pulp (TMP) process streams: pressate water from an Impressafiner and process water from chip washer by using a flotation technique (Dissolved Air Flotation, DAF). The aim of this study was to clarify to what extent aggregated lipophilic extractives can be removed from TMP process water by using dissolved air flotation.

4.3.1 Diffrences in chemical composition of Impressafiner pressate water and process water from chip washer

Characterization of both processes waters given in *Table 4-2* indicate that the main difference between the Impressafiner pressate water and the chip washer water was the concentration of carbohydrates. The water used for washing the chips in the Skogn mill is water recirculated from the disk filter while the water used inside the Impressafiner is white water comming from paper machine. This may be an explanation for why the concentration of carbohydrates was higher in the chip washer than in the Impressafiner pressate water. This difference in carbohydrates concentration seems to have an effect on the flocculation efficiency of colloidal extractives with polymers. Moreover, it was observed that Impressafiner pressate water contained higher concentration of resin acids compared to process water from the chip washer.

Table 4–2: Concentration of extractives, carbohydrates and lignans in process water from the Impressafiner and chip washer.

Substances	Impressafiner pressate water Concentration mg/l	Chip washer Concentration mg/l
Fatty acids	112	86
Resin acids	299	119
Lignans	195	231
Sterols	29	33
Steryl esters	63	91
Triglycerides	108	107
Carbohydrates	1616	2785

The differences in the concentrations of lipophilic extractives (*Table 4-2*) could be explained by the Impressafiner conditions (i.e. high compression ratio inside the Impressafiner).

4.3.2 Efficiency of dissolved air flotation

The efficiency of the flotation technique was evaluated by measuring the turbidity, chemical oxygen demand (COD), the amount of extractives and carbohydrates present in the subnatant and amount of lignin.

Figure 4.11 and *Figure 4.12* summarize the flotation efficiency in terms of reduction of extractives in the subnatant after flotation, for Impressafiner pressate water.

A single component system poly-DADMAC showed the lowest removal efficiency (34%). The probable explanation may be reaction with dissolved carbohydrates and thus be partially consumed before it neutralizes and flocculates the extractives. Therefore, higher concentration of poly-DADMAC was necessary for flocculation of colloidal extractives (*Figure 4.11*). The selectivity of poly-DADMAC to react first with dissolved carbohydrates has been previously showed in the literature (Sundberg A. et al 1993). Another possible explanation is that poly-DADMAC form compact flocs that are too small to be efficiently removed from the process water by flotation.

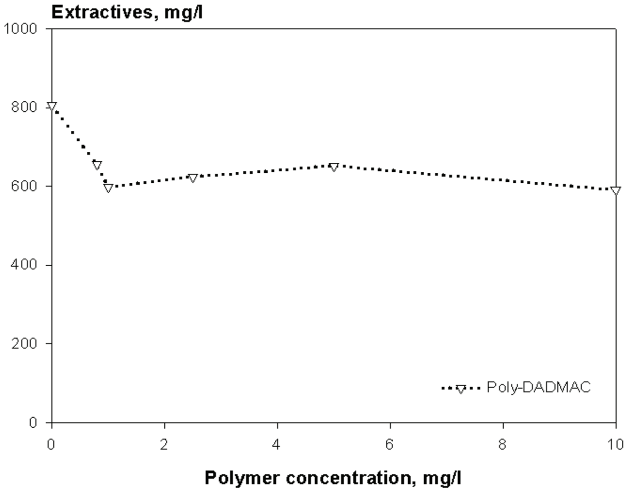

Figure 4.11: The amount of lipophilic extractives in Impressafiner pressate water after DAF (Poly-DADMAC).

On the other hand the higher removal efficiency of C-PAM (65%) can be due to the flocculation mechanism, *Figure 4.12*. C-PAM induces bridging flocculation mechanism, the flocs are larger and they are not that sensitive to polymer dosage but the flocs may be desintegrated by to strong mixing.

The combination of the polymers (poly-DADMAC + C-PAM) showed the highest removal efficiency (78%) for both processes waters (the polymer with the highest ability to remove dissolved and colloidal substances) in terms of total amount of lipophilic extractives in the subnatant after DAF, see *Figure 4.12*. The high removal efficiency could be explained by a combination of flocculation mechanisms charge neutralization and bridging flocculation. The different flocculation mechanisms were described in our previous paper (**Paper II**).

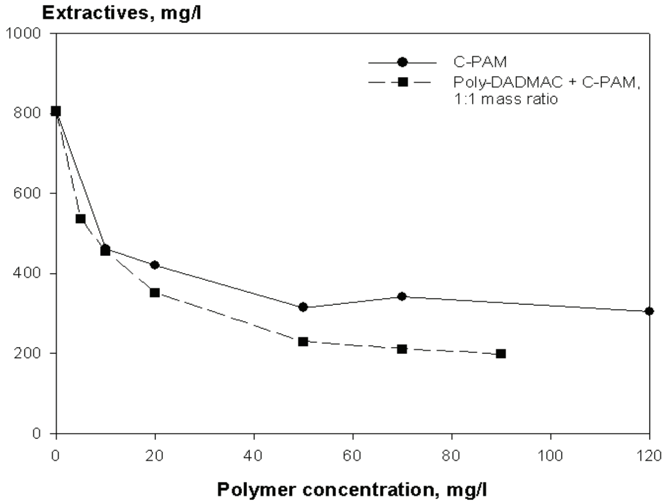

Figure 4.12: The amount of lipophilic extractives in impressafiner pressate water after DAF, C-PAM and combination of the polymers.

4.3.3 Particle size distribution

Measurements of particle size distribution of the pressate water from Impressafiner before and after DAF (*Figure 4.13*) confirm that the polymers used in our study flocculate the lipophilic extractives.

The results show that large flocs in the range of 100-1000 µm are efficiently removed by DAF. After addition of the flocculating polymers and DAF the particle concentrations were much lower and the particle size distribution was dominated by particles in the range 0.1-100 µm that were too small to be removed from the process water by DAF.

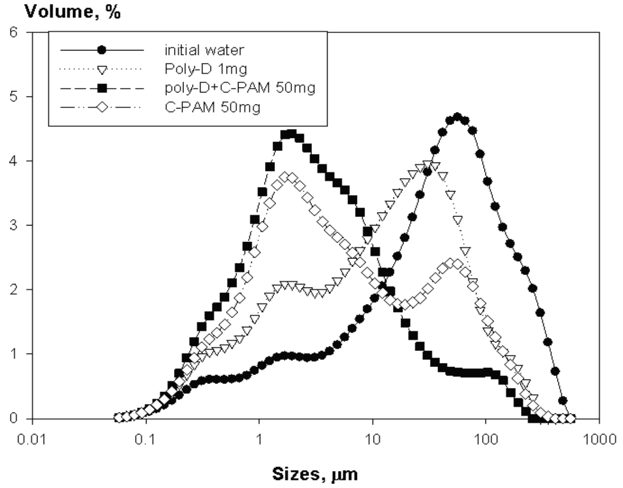

Figure 4.13: Particle size distribution measured for initial Impressafiner pressate water and in Impressafiner pressate water after DAF.

4.4 Removal of dissolved and colloidal substances in water from compressive pre-treatmentof chips using dissolved air flotation. Pilot trial (Paper IV)

The dissolved air flotation laboratory tests results presented in **Paper III** have shown that the combination of the polymers (poly-DADMAC + C-PAM, mass ratio 1:1) gave the best results, both in the flocculation of colloidal extractives present in the process water and in the efficiency after DAF. Therefore a pilot trial in a paper mill has been conducted for assessing the potential benefits of DAF in mill scale.

Paper IV reports on an investigation of the removal of dissolved and colloidal substances in water from compressive pre-treatment of wood chips (Impressafiner pressate water) using a pilot dissolved air flotation (DAF) unit in a paper mill. In order to simulate real DAF process conditions, the fresh Impressafiner pressate water samples were collected and used directly in the pilot dissolved air flotation trial at the mill side.

4.4.1 Characterization of process water

The pressate water samples were collected from the equipment used for pre-compression of chips (Andritz 500 D Impressafiner) in the TMP B line at Holmen Paper Braviken mill, Sweden and used directly in the pilot dissolved air flotation trial at the mill side. The air saturated water used in the pilot DAF trial was pressurized water from the DIP plant at the mill. This water was analysed and found to contain some extractives, carbohydrates and lignin, but the amounts were much smaller than those in the water from the Impressafiner. The characterization of the Impressafiner pressate water and pressurized water used in the DAF pilot trial is given in *Table 4-3*.

Table 4–3: Characterization of the Impressafiner pressate water and pressurized water.

	Impressafiner pressate water	**Pressurized water**
pH	6.6	7.1
Temperature, ^{o}C	135	70
Residual turbidity, NTU	711	20
COD, mg/l	6050	2383
Lignin, mg/l	582	352

Moreover the concentration of extractives and carbohydrates in the process water from an Impressafiner and pressurized water was determined, see *Table 4-4*. More details about the DAF pilot trial are given in **Paper IV**.

Table 4–4: Concentration of extractives, carbohydrates and lignan in process water from Impressafiner and pressurized water.

Dissolved and colloidal substances	Impressafiner pressate water, mg/l	Pressurized water, mg/l
Fatty acids	56	16
Resin acids	204	19
Lignans	143	78
Sterols	20	8
Steryl esters	44	8
Triglycerides	48	0
Carbohydrates	1434	554

4.4.2 Dissolved air flotation efficiency

The flotation efficiency was evaluated by measuring the turbidity, chemical oxygen demand (COD), the amounts of extractives, carbohydrates and lignin present in the subnatant before and after flotation.

Figure 4.14 and *Figure 4.15* summarizes the flotation efficiency in terms of reduction of extractives in the subnatant after flotation for Impressafiner pressate water. In the graphs and in the calculations, the amount of dissolved and colloidal substances added with the pressurized water is taken into account.

When Poly-DADMAC (*Figure 4.14*) was used alone as flocculation agent, the total amount of lipophilic extractives was reduced by about 45% at a polymer concentration of 2.5 mg/l. The concentration was not further reduced by adding up to 20 mg/l Poly-DADMAC.

When C-PAM was used as flocculation agent for Impressafiner pressate water the total amount of lipophilic extractives was reduced by more than 70% already at a polymer concentration of 10 mg/l. Adding more polymer slightly increased reduction to reach 75% at a polymer concentration of 75 mg/l. C-PAM in combination with Poly-DADMAC (1:1 mass ratio) behaved roughly in the same way as C-PAM alone and gave the best reduction in total amount of lipophilic extractives for Impressafiner pressate water (76%) at polymer concentration 50 mg/l, see *Figure 4.15*.

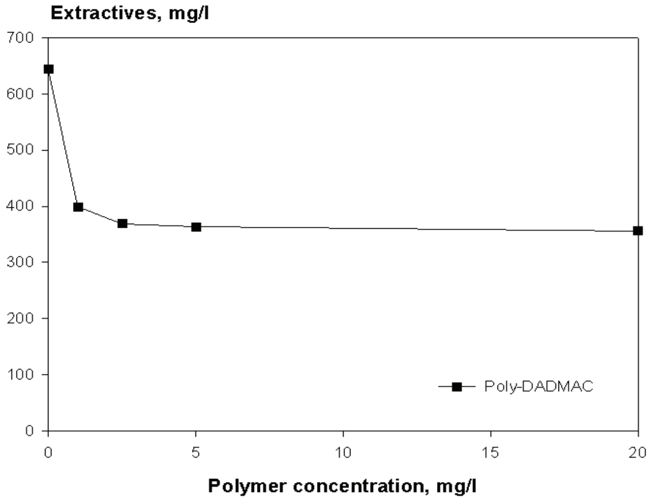

Figure 4.14: The amount of lipophilic extractives in Impressafiner pressate water after DAF (Poly-DADMAC).

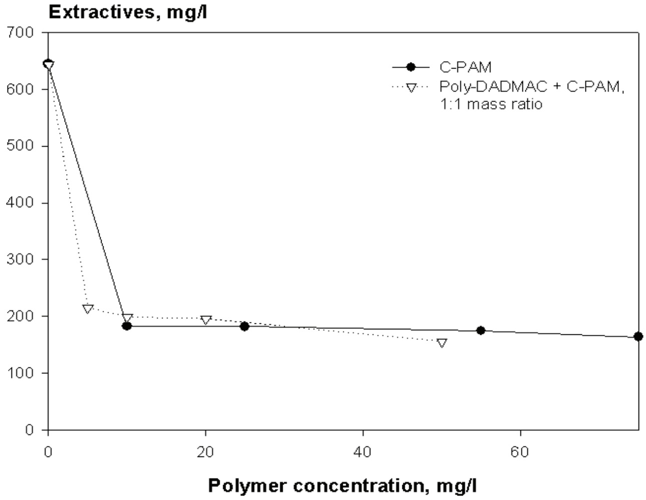

Figure 4.15: The amount of lipophilic extractives in Impressafiner pressate water after DAF (C-PAM and combination of the polymers).

The results from pilot DAF trial are qualitatively in agreement with those obtained previously in laboratory scale experiments with Impressafiner water taken from the same mill. Quantitatively there are differences between the experiments that yield some insight into the flocculation mechanism. For more details, see **Paper IV.**

4.4.3 Effect of pH and temperature on the dissolved air flotation efficiency

In the pilot DAF trial the pH of the Impressafiner pressate water was 6.6 which was higher than in the laboratory tests (pH 5.5). Moreover, the air-pressurized water used in the pilot trial had high pH (pH 7.1). It was shown by Sundberg et al. (2009) that the pH of the process water affects not only the degree of dissociation of the carboxyl group but also determines the phase distribution of fatty and resin acids between the water phase and the colloidal phase, see *Figure 4.16*.

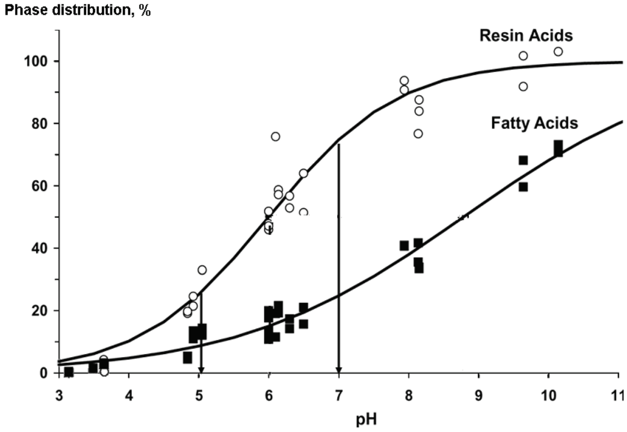

Figure 4.16: Phase distribution of fatty and resin acids (adapted from Sundberg et al. 2009).

Our pilot DAF results show that Impressafiner pressate water contained higher amount of the dissolved extractives (17-20%) compared with laboratory results (13-15% dissolved extractives). It seems that the phase distribution of extractives affect the efficiency of DAF. In agreement with our results, Richardson and Grubb (2004) have shown that the phase distribution of extractives between fibre bound, colloidal and dissolved affect the efficiency of DAF and that the fibre bound and colloidal extractives can be removed with a removal efficiency of 80-90%. However, the dissolved extractives were removed with a very low efficiency 30%.

The temperature of the Impressafiner pressate water may also affect the efficiency of DAF. Experiments in the pilot trial were carried out at 70°C while laboratory experiments were carried out at 25°C. Negro et al (2005) noted the solubility of air in the pressurized water will be lower at higher temperature. This may also contribute to the lower removal efficiency at the higher temperature. For example, at 6 bar the amount of air in saturated water at 20°C is 36% higher than the amount at 40°C (Ross et al. 2000).

On the other hand, the higher temperature of the process water implies that the kinetics of the flocculation (collision rate) is faster.

4.4.4 Effects of COD removal on effluent water

Chemical oxygen demand (COD) is a common parameter used for characterization of organic substances present in paper mill process water and effluents. The reduction in the COD involves the removal of negatively charged particles present in the TMP process water. Thus, the removal of wood extractives significantly contributes to COD reduction.

It is known from the literature that washing mechanical pulp (i.e. disc filter, screw presses, etc) is a good way to reduce the COD and extractives content in the pulp, but in this case fibre recovery equipment is needed (Käyhkö 2002; Braeuer et al. 2008). Fibre recovery implies that the fibre bound extractives are recirculated into the process, thus rendering removal of extractives less efficient.

A theoretical mass balance was calculated knowing the consistency of the pulp passing through a screw press, which is generally assumed to be 5-6%, see *Figure 4.17*. In the press the pulp is dewatered to approx. 28-30% consistency. The filtrate from the screw press, having a consistency of approx. 0.6%, typically contains about 4000-6000 mg/l COD. Thus, for a TMP mill with a production of 700 t/d, it was found that screw press squeezes out high volume of water: the flow of the filtrate from screw press will be approx. 110 l/s and the amount of filtrate will be about 9500 t/d.

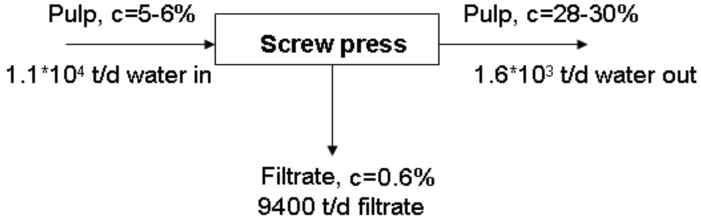

Figure 4.17: Theoretical mass balance calculation around a screw press.

On the other hand, with compressive pre-treatment of the chips, using an Impressafiner, it is possible to remove extractives from the wood chips before refining, thus reducing the amount of extractives that enter the pulping and papermaking process. Thus the removal of dispersed extractives can be done from water containing very few fibres. For a TMP mill using as raw material Norway spruce, with a production of 700 t/d, it was found that the combined water flow from Impressafiner + Plug Screw is approx. 16 l/s, i.e. the amount of water will be about 1382 t/d, see *Figure 4.18.* The water contained approx. 6700 mg/l COD. This water was found to contain a substantial amount of extractives (about 15% from the total amount of extractives in the chips). These were mainly resin acids which thus could be removed from the chips at an early stage into a small volume of water, while fatty acids remained in the chips (Tanase et al. 2010).

Resins acids are generally regarded as the main acute toxicity contributors in TMP effluents (Magnus et al. 2000).

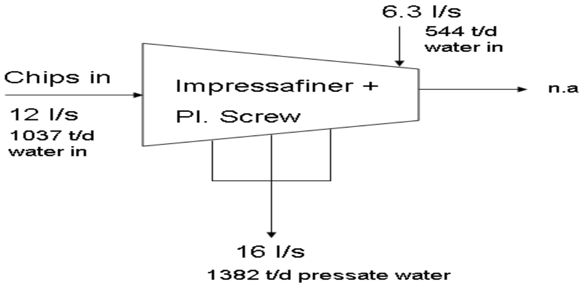

Figure 4.18: Impressafiner water flow

When using either a screw press or an Impressafiner, the COD and extractives are transferred from the chips/pulp into the process water. Both filtrates from screw press and pressate water from Impressafiner can be sent to a DAF unit, in order to reduce the amount of extractives and COD from the process water, before the water is sent to the effluent treatment or reused internally in the mill. However, the difference is that a screw press generates a high volume of water which implies lower efficiency in DAF and higher amounts of COD and resin acids that are sent to the effluent treatment. Reducing COD with one tonne in an effluent plant requires about 1 MWh of energy. Therefore, an effective DAF can reduce the energy needed in the effluent plant. Moreover, large volumes of the process water imply large investments cost for DAF unit and for the flocculation chemicals.

Having a concentrated water stream, such as Impressafiner pressate water, the COD and the amount of extractives are reduced in the beginning of the process, before refining. As a consequence, treatment of Impressafiner pressate water can be done by using small amounts of polymer and smaller DAF unit. Moreover, by reducing the amount of extractives from chips into the water phase and by using DAF unit for treatment of concentrated water stream, the energy consumption required for running a DAF unit is reduced seven times compared with using a DAF unit for treatment of water from a screw press. Thus the total cost is reduced and DAF efficiency is improved.

Chapter

5

CONCLUSIONS

From the results of mass balance calculations around an Impressafiner (**Paper I**), it may be concluded that by using a compressive pre-treatment of wood chips up to 40% of the lipophilic extractives can be removed before the refining process. As a consequence, the amount of extractives that enter the pulping and papermaking process is reduced. However, handling of the process water is required in order to reduce the amount of wood extractives before the water is recirculated in the mechanical pulp process or before the water is sent to the effluent treatment.

The amount and phase distribution of wood extractives in process water affect the efficiency of cationic polymers and the efficiency of DAF respectively. The second part of the work (**Paper II**) was focused on the investigation of the effects of cationic polyelectrolytes on the interactions with colloidal extractives in the process water. The study was limited to the use of two different polymers and combination of them (mass ratio 1:1). It was found that the polymers used in our study, efficiently flocculate the colloidal extractives present in the process water via two different flocculation mechanisms: charge neutralization and bridging flocculation. Particle size distribution and Turbiscan measurements yielded additional informations on the way the polyelectrolytes flocculated the colloidal extractives. Neither kinetic aspects of the interactions nor floc strength were studied.

In the third part of the thesis (**Paper III** and **Paper IV**), a dissolved air flotation (DAF) unit was used to remove flocculated extractives from the process water. The work was limited to an investigation of two different cationic polymers and combination of them. The removal efficiency depends highly on the type of flocculating polymer used. In practice, the optimization of coagulation and flocculation is necessary for optimum performance of flotation system. The cationic polymers used to flocculate the colloidal extractives before actual flotation, showed selectivity for the carbohydrates dissolved in the process water. As a result, the dissolved air flotation efficiency is affected. Experimental results indicate that pH and the temperature of the process water affect the dissolved air flotation efficiency. It was found the large flocs in the range of 100-1000 μm are effieciently removed by DAF. Moreover, by using DAF the fibre bound and colloidal extractives could be removed with a removal efficiency of 80-90%.

In conclusion, the goal of this study to reduce the amount of extractives from the wood chips before refining and reduce the energy consumption during subsequent refining was achieved. Further, it seems that DAF is a convenient method to use for removing the flocculated extractives from concentrated process water streams. Thus there is the possibility to recover extractives from the sludge and to use them in synthesis on new molecules, bioactive chemicals, solid fuel, pharmaceuticals.

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Paper I

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MASS BALANCE OF LIPOPHILIC EXTRACTIVES AROUND IMPRESSAFINER IN MILL AND PILOT SCALE

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KEYWORDS: Thermomechanical pulping, Extractives, pine, spruce, Dissolved colloidal substances

SUMMARY: Removal of extractives from the pulp furnish is of great importance for the improvement of paper machine efficiency and also for reducing the energy consumption during the thermomechanical pulp refining process. Extractives can exist in many different forms in the process water; as colloidal particles, dissolved or attached to fines and fibres. It is therefore important to know in which form they exist in order to fully understand their behaviour. In this paper, we report on an evaluation of the removal of extractives released from chips of different raw materials pre-treated in an Impressafiner, in pilot and in mill scale. In pilot trial the raw materials used were loblolly pine (Pinus Taeda) and white spruce (Picea Galuca) and in the mil scale trial the raw material used was norway spruce (Picea Abies). The colloidal stability of extractives present in the pressate water from the Impressafiner and their flocculation behaviour by cationic polymers (C-PAM and Poly-DADMAC) under different conditions was also investigated. Calculations of mass balances around an Impressafiner showed that it was possible to remove up to 40% of extractives before the refining process. The reduction in total extractives content was mainly due to released resin acids while fatty acids, triglycerides, steryl esters and sterols to a large extent remained in the wood chips after pre-treatment. The removal of extractives from pine was four times higher than from spruce chips. The results can be explained in terms of the extractive composition in the raw material and the morphological differences in the wood structure.

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The Impressafiner compresses and delaminates the chips while squeezing out water. The purpose of this treatment is to open up the wood structure before refining, to minimize variation in moisture content, maximize the removal of extractives, reduce variation in bulk density and reduce the energy consumption during subsequent refining.

The Impressafiner is designed to compress the chips to a uniform size distribution as they proceed to the discharge of the compression screw press. The structural changes in the wood chips accelerate and improve the uniformity of heating, thus allowing a reduction in time required to soften the wood. The high compression squeezes out extractives and dissolved organic substances. Special attention has to be given to the retention time and pressure. High pressure and long retention time typically results in an increase in pulp strength but a decrease in pulp brightness (undesirable darkening reactions) (Sabourin et al. 2002).

The intensive mechanical action that the chips undergo in the Impressafiner and in the subsequent refiners leads to "breakage" of cells which contain wood extractives and to the release of material into the process water. This material is commonly divided into dissolved and colloidal substances (DCS) (Rundlöf and Wågberg 2004). The material dissolved in the process water consists mainly of wood polymers, such as hemicelluloses, pectins, low molecular mass lignin fragments and lignans. Water-insoluble resin is mainly dispersed into the process water as colloidal droplets (Stenius 2000). The colloidal particles contain lipophilic wood extractives. The main components of these are fatty acids and their glyceride esters (fats), terpenes and terpenoids including resin acids, sterols and their fatty acid esters, and waxes (Rundlöf and Wågberg 2004).

The droplets form stable colloidal dispersions, which do not aggregate even at high salt concentration (Sundberg K. 1995). This stability is due to steric stabilization conferred by dissolved hemicelluloses, mainly mannans, which accumulate around the droplets. This prevents them from aggregating even when the repulsive electrostatic interactions (at high salt concentration) become insignificant (Allen 1979; Swerin et al. 1993; Holmbom and Sundberg A. 2003). In the hemicellulose-free dispersions the colloidal wood resin (extractives) are electrostatically stabilized and may be destabilized by the addition of simple electrolytes (Sundberg K. et al. 1996).

A few reports have been published regarding removal of extractives during compression of chips in a screw feeder (Cisneros and Drummond 1995; Thornton and Nunn 1978). Cisneros and Drummond (1995) report on how and to what extent wood resin was liberated when lodgepole pine chips were compressed in a plug screw feeder. They found that increasing the compression ratio from 3:1 to 5:1 results to an 18% decrease in the number of resin containing cells. However, this study was made on a screw press without pressurized conditions like those in the Impressafiner.

A mass balance of resin acids in the mill after the first stage refining is reported by Peng and Roberts (2000). Their results indicate that the pimaric type resin acids in the wood and pulp remain almost the same during process, while the amount of abietic type resin acids changes during the process. There is a particularly significant change during the first refining stage. Moreover, they found that the resin acids were dispersed as colloidal particles as well as dissolved in the process water.

The extractives removed from the Impressafiner will be concentrated in the pressate water. Handling of this water is important in order to avoid that the extractives enter the effluent treatment. Thus, extractives from the pressate water should be removed, which could be done e.g., by flocculation and flotation.

One way to remove extractives is washing of the pulp (wash filter or filter presses) (Käyhkö 2002), but in this case fibre recovery equipment is required. On the other hand, with compressive pre-treatment of the chips, using an Impressafiner, it is possible to remove extractives from the wood chips before refining, thus reducing the amount of extractives that enter the pulping and papermaking process, without loss of fibres. In some cases the total energy consumption during subsequent refining can also be reduced.

The objective of this study was to investigate the possibility to remove extractives released from chips in Impressafiner equipment and to determine the mass balance of extractives around a mill scale Impressafiner installation. The amount and composition of extractives released to the pressate water was related to the production of chips through the Impressafiner. Different raw materials were investigated and further analysis of the pressate water from the Impressafiner was also undertaken.

We also report a preliminary study of the flocculation of colloidal extractives with cationic polymer at the native pH of the pressate water from Impressafiner (pH 5.5). The results of a more detailed study will be presented in a forthcoming paper.

MATERIALS AND METHODS

Pilot scale trials

Raw material

Freshly cut loblolly pine (*Pinus Taeda*) pulpwood-size logs were obtained from South Carolina (U.S.A.) and white spruce (*Picea Glauca*) was obtained from a forest in the Wisconsin (U.S.A).

Impressafiner

The experimental work was conducted at the Andritz Research and Development Center in Springfield, Ohio. The Impressafiner operating conditions in pilot scale were: compression ratio 5:1(increase from the inlet to the discharge of the screw press), pressure 1.4 bar, temperature 125^{o}C, retention time 15 s. The production rate in the pilot scale Impressafiner was 18 – 19 ton/d. The Specific Energy Consumption (SEC) was about 40 kWh/ton.

Both pre-treated chips and pressate liquors were collected and they were analyzed for the amount and composition of extractives.

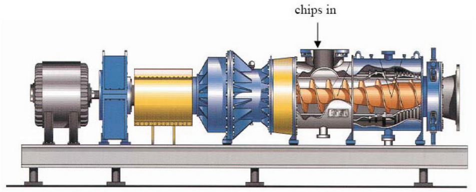

Figure 1. Andritz MSD 500 Impressafiner

Mill scale trials

Raw material

Norway spruce (*Picea Abies*) pulpwood-size logs were used in Holmen Paper Braviken mill, Sweden.

Impressafiner

An Impressafiner (Andritz Impressafiner MSD 500) system (Figure 1), installed at Holmen Paper Braviken mill in August 2008, was used in the mass balance study. The Impressafiner operating conditions were: compression ratio 5:1 (increase from the inlet to the discharge of the screw press); pressure 0.5 bar, temperature 111^{o}C, retention time 15 s. In the mill scale trials both pretreated chips and pressate liquors were collected and analysed for extractives content and composition. The Specific Energy Consumption (SEC) in mill scale Impressafiner is 20 kWh/ton, having a production rate of 30 ton/h.

Chemicals

Poly-(N,N-dimethyl-3,4-diethyl pyrrolidonium chloride), Poly-DADMAC, with high charge density (CD) and low molar mass (M_w) and cationic polyacrylamides, C-PAM, Poly-(Trimethyl-3-methacrylamidopropyl-ammonium chloride) with high molar mass (M_w) and low charge density (CD) (Kemira Oyj, Finland), were used as flocculants of colloidal extractives in the process water (Table 1).

Table 1. Properties of the cationic polymers used, Poly-DADMAC and C-PAM

Substance	M_w 10^6g/mol	CD meq/g	DS* mol-%
Poly-DADMAC	0.17	6.2	100
C-PAM	14	0.3	2

*DS, degree of substitution, is the percentage of monomers carrying a charged group

Experimental methods

Water samples were collected from TMP B line, Holmen Paper Braviken mill, Sweden. The raw material was 100% norway spruce. The sampling points are schematically shown in Figure 2.

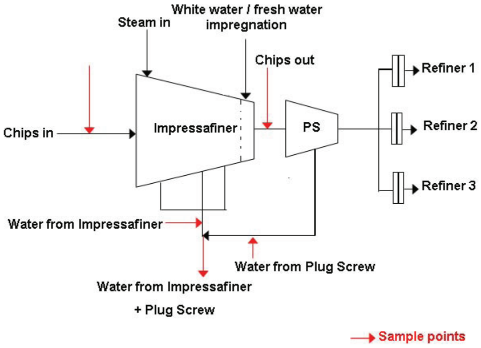

Figure 2. Sampling points around Impressafiner in Holmen Paper Braviken mill

The pressate samples were analyzed as fresh as possible for the extractives content and composition. Furthermore, the solubility, colloidal stability and flocculation of the extractives in the pressate water under different conditions were determined.

The stability of colloidal substances can be studied, for example, in terms of their aggregation behaviour in the presence of simple electrolytes / polyelectrolytes. The loss of colloidal stability is defined as electrolyte induced aggregation of dissolved colloidal substances (DCS) and the subsequent sedimentation of the aggregates by gravity centrifugation (Sundberg K. 1995; Sundberg K. et al. 1996)

The stability of dispersed wood resin against flocculation was studied by turbidity measurements before and after addition of salt or polymers. Turbidity was measured as Nephelometric Turbidity Units (NTU) as function of the amount of polymer needed for flocculation of extractives. Different concentrations of salt / polymers were added to the suspension of colloidal extractives, mixing 1 min with a magnetic stirrer before centrifugation (1500g, 10 min). The turbidity was measured before centrifugation and also on the supernatant after centrifugation. Thus, the turbidity values may increase in some cases upon formation of small aggregates (flocs). Also, suspensions of extractives that differ in colloidal size distribution will differ in their measured turbidity values at a given resin concentration.

The Chemical Oxygen demand, COD, was measured according to the Dr. Lange method (ISO 6060-1989). The amount of carbohydrates was determined using the method described by Chaplin and Kennedy (1986). The pressate water from Impressafiner (1ml) was mixed with 1 ml phenol solution (5g/100ml) and 5 ml concentrated acid sulphuric (96%). Thereafter, it was allowed to cool down for 10 minutes, mixed well and left for cooling for 30 minutes. The total amount of carbohydrates is determined by measuring the absorbance at 490 nm, using plastic kyvettes.

The dissolved and colloidal fraction after centrifugation at 500g for 30 min. was collected. The dissolved fraction was separated by ultrafiltration using an Amicon cell with a 0.1μm filter. The amount and composition of extractives in wood chips and pulps were determined by extraction with a cyclohexane:acetone mixture (9:1) according to SCAN-CM 67:03, followed by GC analysis. The amount and composition of extractives in process water were determined by extraction with MTBE, using the method described by Örså and Holmbom (1994).

For the pilot trials, the mass balance of the total amount of extractives removed from the chips was calculated based on the flows and concentrations around the Impressafiner.

RESULTS AND DISCUSSION

The results from pilot scale trials (Table 2) show that by using an Impressafiner it was possible to reduce the total amount of extractives, including fatty acids, resin acids, triglyceride, and steryl esters which enter in the first stage refiner. The amount of sterols was not reduced. The results show that it was mainly resin acids that could be removed while the fatty acids to a large degree remained in the chips. The results also show that a much larger fraction of the extractives were removed from pine than from spruce chips.

Table 2. Removal of extractives from chips through Impressafiner in pilot scale

Raw material	Total fatty acids*, %	Resin acids, %	Total extr. removed, %
Loblolly pine	8	65	40
White spruce	4	38	10

*Total fatty acids include fatty acids, steryl esters and triglycerides

The difference in the results between pine and spruce shown in Table 2 may be due to the morphological difference found in pine and spruce wood. Table 3 shows the difference in extractives location in pine and spruce wood. Extractives in resin canals are easy accessible in chips and can be dispersed or dissolved during compression, while extractives in parenchyma cells are not easy accessible (Cisneros and Drummond 1995). The extractives in pine are up to 70% located in resin canals, while in spruce only about 45% of the extractives located in resin canals (Back and Carlson 1955).

Furthermore, in pine the resin canals are 50 to 200 µm in diameter while in spruce species, the resin canals are 30 up to 100 µm (Back 2000). The resin canals are lined with thin-walled epithelial cells which secrete resin into the canals. In southern pines, longitudinal parenchyma cells partially surround most longitudinal resin canals. Most longitudinal parenchyma cells are thin-walled; thick-walled specimens are occasionally found (Koch 1972).

Table 3. Location of extractives in pine and spruce wood (Back and Carlson, 1955)

Raw material	Extractives in resin canals, %	Extractives in parenchyma cells, %	Average of pit wall area, %
Pine	70	30	50
Spruce	45	55	5

In pines, the pressure in the resin canals is high; it has been evaluated to be in the range of 7 to 12 bars. Moreover, the average pit wall area is higher in pine than in spruce. The pit size and distribution in the wood affects the deresination rate in mechanical pulping process (Back 2000). The epithelial cells within the canals are thin-walled and unlignified in the sapwood, and the canal resin is quickly pressed out. In spruce species, the epithelial cells are more thick-walled and lignify earlier. In spruce, the pressure in resin canals is high only in the young part of the sapwood (i.e. the outer most 3-5 annual rings) (Engström and Back 1959). These differences offer an explanation for the different degree of extractives removal shown in Table 2.

Figure 3 shows a Scanning Electron Microscope (SEM) image of a resin canal in a chip from pine before passing the Impressafiner. Figure 4 shows the wood structure in a chip after passing the Impressafiner.

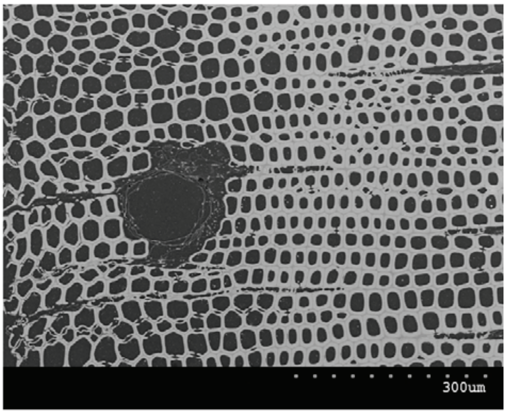

Figure 3. Typical SEM image of loblolly pine chips before Impressafiner

Thus the SEM images confirm that during chip compression resin canals in pine are crushed and the resin is released.

From the SEM images of white spruce chips (Figure 5) it is obvious that the chip structure is opened up but the fibres are mostly intact and the parenchyma cells are also to a large degree intact after passing through Impressafiner.

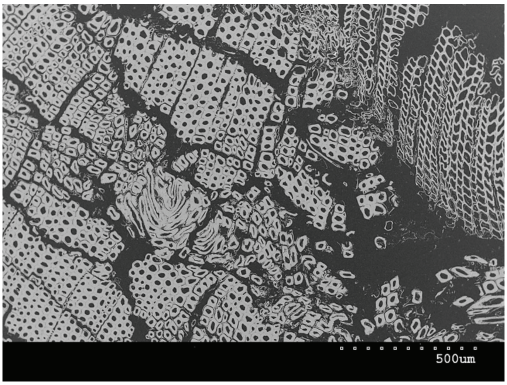

Figure 4. Typical SEM image of loblolly pine chips after Impressafiner

There are fundamental differences between extractives in resin canals and parenchyma cells, and also between the extractives in sapwood and in heartwood, both with regard to physical accessibility and chemical composition. While neutral fats including fatty acids dominate the sapwood of both pine and spruce, the amount of resin acids and fatty acids are higher in the heartwood of pine (Back 2000).

Figure 5. SEM image of white spruce chips after Impressafiner

Cisneros and Drummond (1995) found that more than 70% of the parenchyma cells in pine remained intact after chip compression; while more than 90% of the parenchyma cells were damaged after 1st stage refining. Thus, extractives both from resin canals and parenchyma cells were liberated after the primary refining stage, but there may have been a preferential liberation from resin canals during chip compression.

Fernando et al. (2008) found that the triglycerides content, fatty acid content and resin acid content were significantly higher in pine than in spruce, while the content of steryl esters was about the same in both wood species. From a study of the adsorption of extractives onto fibre surfaces after refining, Furthermore, they conclude that the inferior strength properties shown by pine TMP pulps compared with those of spruce may to some extent be caused by the presence of higher amounts of extractives (especially triglycerides) on the surface of pine fibres.

The analysis of extractives both from pilot and mill scale (Table 2 and 4) shows that resin acids, located in the resin canals, can effectively be removed from chips in the Impressafiner, while the extractives localized in parenchyma cells to a large degree remains in the chips. This can also be seen from the SEM images (Figure 5) where resin canals are destroyed after passing the Impressafiner while the parenchyma cells seems to remain more or less intact (Figure 4). This is in agreement with what Cisneros and Drummond (1995) found for lodgepole pine that has passed a screw feeder with a compression ratio of 5:1. Thus the difference between the amounts of extractives released from spruce and pine conform to the differences in amounts and composition found by Persson et al. (2005) and Fernando et al. (2008).

Table 4. Amounts of extractives and carbohydrates in pressate water from Impressafiner in mill scale

Raw material – Norway spruce	
Dissolved colloidal substances	
	Concentration, mg/L
Fatty acids	**129**
Resin acids	**154**
Lignans	**189**
Sterols	**27**
Steryl esters	**54**
Triglycerides	**61**
Carbohydrates	**1470**

Mass balance

The results from the mill scale trial showed a reduction in free fatty acids by 7%, resin acids 35%, steryl esters 10%, triglycerides 7% and sterols 10%. Moreover, the composition of the pressate water from the Impressafiner indicates that it was mainly resin acids that could be removed while the fatty acids, steryl esters and triglycerides to a large degree remained in the chips (Table 4).

A mass balance for extractives was calculated from the flows around the Impressafiner (Figure 6). The extractive content was measured in the white water used for impregnation and in the chips coming into the Impressafiner. Also, water and chips coming out of the Impressafiner, and water from the plug screw were analyzed for extractive content. In the Impressafiner 2 ton/d of extractives were introduced with the chips and 0.02 ton/d extractives were introduced with white water used for impregnation in the end of the Impressafiner. By measuring the extractives content coming out from the Impressafiner it was found that 1.7 ton/d extractives were carried out into the plug screw with the chips, 0.2 ton/d extractives was transported into the pressate water from the Impressafiner and 0.2 ton/d extractives were ejected in the water from the plug screw.

The results from the mass balance show a removal of 15% extractives from norway spruce. This is higher than the 10% achieved in earlier pilot-scale studies of white spruce.

Removal of extractives from process water

Using an Impressafiner substances contributing to Chemical Oxygen Demand (COD) and/or extractives are efficiently squeezed out, creating more favourable conditions in the water systems of the pulp and paper mill. Moreover in the COD from the Impressafiner there will be very few fibres. Thus one advantage of using an

Impressafiner is that removal of dispersed extractives can be done from water containing very few fibres.

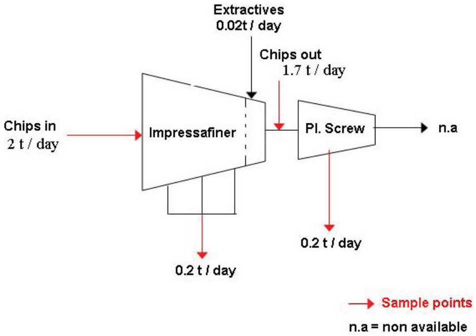

Figure 6. Mass balance of extractives around Impressafiner in Holmen Paper Braviken mill

SEM images of the chips after pre-treatment shows that their structure is opened up and to some extent defibrated (Figure 5). The high compression level in the Impressafiner, in addition to inducing maceration of the wood chips also results in the production of some broken fibres and fines. Thus the extractives removed from chips in the Impressafiner are attached to the fines, occur as colloidal particles or are dissolved. Determination of the different physical forms of extractives present in the pressate water is important in order to optimize the process of removing them from the pressate water.

The results from the mass balance show that 30-40% of extractives in the pressate water from the Impressafiner at the Braviken mill were attached to fines and fibres, 40-50% of the extractives were in colloidal form, and only 10-13 % of the extractives were dissolved.

The stability of dispersed wood resin against salt induced aggregation can be evaluated by simple turbidity measurements. The lipophilic extractives in unbleached samples remained relatively stable in the presence of electrolytes; little aggregation resulting in sedimentation by centrifugation occurred (Figure 7).

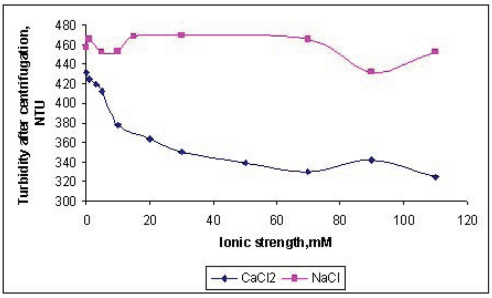

Figure 7. Residual turbidity after addition of salt to pressate water from Impressafiner

Turbidity of supernatant after centrifugation of wood extractive suspensions to which NaCl or $CaCl_2$ had been added at pH 5.5 shows their effect on the colloidal stability of the extractive suspension. Although the turbidity was slightly lowered by adding $CaCl_2$, the effect of the electrolytes is not the one expected for electrostatically stabilized colloids. If the colloidal extractives were stabilized only by electrostatic repulsion they should typically coagulate at an addition of 100 mM NaCl or a few mM $CaCl_2$ (Hiemenz 1986). Our results are in agreement with previous results suggesting that steric interactions stabilize colloidal wood resin particles (Allen 1979; Pelton et al.1980; Sundberg K. et al. 1994).

It has been shown that colloidal extractives present in the process water from mechanical pulp are sterically stabilized by dissolved polymers, originating mainly from wood (Allen 1979; Swerin et al. 1993; Sundberg K. 1995). Steric stabilization of colloidal wood extractives is strongest in process waters from unbleached thermomechanical pulp (TMP). In order to aggregate the sterically stabilized colloidal wood extractives effectively in process waters, either organic or inorganic fixation aids are needed (Sudberg K. et al. 1994). Cationic polyelectrolytes can induce attractive forces, such as bridging, or diminish the electrostatic repulsion by neutralizing the surface charges of colloidal wood resin, thereby increasing the importance of van der Waals forces. In these cases, polyelectrolytes act as flocculants. They can also act as stabilizer, if their adsorption changes the forces between the surfaces to repulsive, such as steric repulsion or electrostatic repulsion due to charge reversal. The role of polyelectrolyte is a matter of dosage (Stenius 2000).

It has been shown that turbidity measurements correlate very well with the concentration of colloidal extractives in water (see Figure 8) (Johnsen 2007; Sundberg A. et al. 1993; Sundberg K. et al. 1994; Sundberg K. 1995; Sundberg K. et al. 1996). Hence, measurements of residual turbidity of the pressate water from Impressafiner, i.e. turbidity measured after centrifugation of flocculated material, were used to follow the effect of coagulants on resin particles.

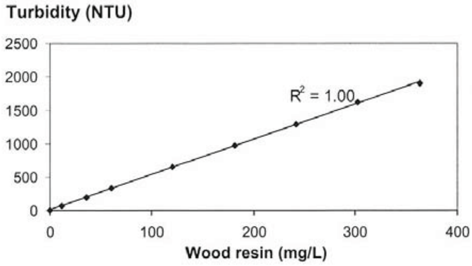

Figure 8. Turbidity of wood resin dispersions at various concentrations of dispersed wood resin (Johnsen 2007)

The study of cationic polyelectrolytes on interaction with colloidal wood extractives in the pressate water from Impressafiner was investigated. In our study, various amounts of cationic polyelectrolytes (Poly-DADMAC, C-PAM and Poly-DADMAC + C-PAM) were used. When Poly-DADMAC was added to the suspension the electrostatic repulsion decreased at low concentration of polymer until it reached the charge neutralization point. This occurred at polymer concentration of 1 mg/l. This effect can also be seen in reduction of residual turbidity after addition of polymer (Figure 9). The same effect can be seen when adding C-PAM and combination of the polymers (Figure 10).

A more detailed study of the flocculation behaviour of extractives present in the pressate water from Impressafiner using cationic polymers will be published in a forthcoming paper.

However, the results show that different cationic polymers can be used to flocculate extractives present in the pressate water from the Impressafiner. Thus, the results suggest that DAF may be a convenient method to remove extractives from the pressate water coming from the Impressafiner, as almost 90% of the extractives are in the fibre-bound or colloidal form. Studies to verify this possibility are in progress.

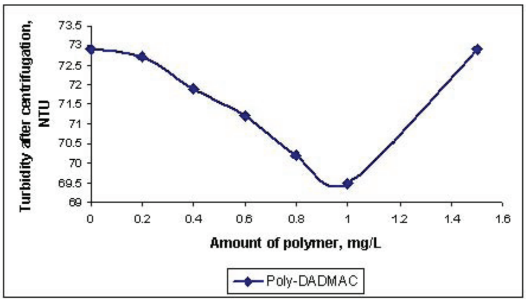

Figure 9. Residual turbidity after addition of Poly-DADMAC to pressate water from Impressafiner

Richardson and Grubb (2004) studied the extractives removal from thermomechanical process water using a Dissolved Air Flotation, DAF, which generally requires flocculation of particles smaller than a few µm before flotation. They found that the fibre-bound and colloidal extractives were removed from the TMP process water with a removal efficiency of 80-90%.

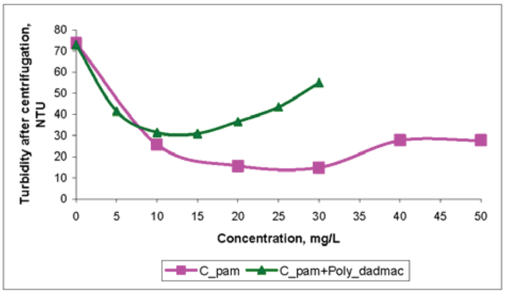

Figure 10. Residual turbidity after addition of cationic polymers (1:1 mass ratio) to pressate water from Impressafiner

CONCLUSIONS

Up to 40% of the lipophilic extractives can be removed from pine and 10% of extractives can be removed from spruce by pre-treatment in an Impressafiner in pilot scale before the refining process. In mill scale trial up to 15% of extractives can be removed from spruce by pre-treatment in an Impressafiner. The reduction in total extractives content is mainly due to release of resin acids while fatty acids, triglycerides, steryl esters and sterols to a large extent remains in the wood chips after pre-treatment. There is a clear difference in behaviour between spruce and pine chips. The amount of extractives present in pine was four times higher than in spruce chips. These differences can be explained in terms of extractive composition in the raw material and the morphological difference in the wood structure.

Using salts the main observation was that the colloidal particles were indeed stable against salt induced aggregation. On the other hand, all polymers used in this study flocculated the colloidal extractives in the process water. However, in practise, care has to be taken in the choice of chemicals and optimizing process conditions.

Acknowledgements

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Paper II

Opedal Tanase M., Stenius P., Johansson L. and Hill J. (2011):
Flocculation of colloidal wood extractives in process water from
precompression of chips in thermomechanical pulping,
Nordic Pulp and Paper Research Jornal, accepted

FLOCCULATION OF COLLOIDAL WOOD EXTRACTIVES IN PROCESS WATER FROM PRECOMPRESSION OF CHIPS IN THERMOMECHANICAL PULPING

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KEYWORDS: Extractives, Flocculation, Turbidity, Turbiscan, Electrophoresis, Particle size distribution

SUMMARY: The aim of this study was to investigate the flocculation of colloidal extractives present in pressate water from an Impressafiner with different cationic polymers. A high charge density and low molar mass polymer (poly-DADMAC) and a high molar mass and low charge density polymer (C-PAM) were used in our study. The results indicate that these polymers efficiently flocculate colloidal extractives present in the process water via two different flocculation mechanisms: charge neutralization and bridging flocculation. Moreover, the results are discussed in terms of turbidity, sedimentation rate (Turbiscan) and particle size distribution of flocculated extractives.

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During production of thermomechanical pulp (TMP) large amounts of wood material are released into the process water. This material consists mainly of wood polymers (hemicelluloses, pectins), wood resin, low molecular mass lignin fragments and lignans. Water-insoluble resin is mainly dispersed into the process water as colloidal particles (Stenius 2000) containing lipophilic wood extractives. The main components of these are fatty acids and their glyceride esters (fats), terpens and terpenoids including resin acids, sterols and their fatty acid esters, and waxes (Ekman and Holmbom 2000).

The organic materials in circulating waters in TMP mills have been well characterized in several studies, since many of the substances are detrimental both to paper quality and the process efficiency (Sjöström 1990; Nylund et al. 1993; Thornton 1993; Back and Allen 2000). Extractives (e.g. resin acids) are generally regarded as the main acute toxicity contributors in TMP effluents (Magnus et al. 2000). Because of this and other environmental concerns, the paper industry is required to reduce their fresh water consumption. However, closing the water circulation system of a paper machine and possibly converting it into a totally effluent-free papermaking process results in a build-up of detrimental substances in the white water. Consequently, the system becomes more sensitive to disturbances and variations in the process. This implies that the white water has to be continuously cleaned (Linhart et al. 1987). Moreover, it becomes necessary to eliminate harmful substances as early as possible in the beginning of the process or at least to decrease their negative effect. Therefore it is important that small process streams with high concentration of organic substances (i.e. extractives) are treated before they reach toxic levels in the process water or before the water is send it to the effluent plant.

One possible way to remove extractives from the wood chips before refining is using a compressive pre-treatment, such as an Impressafiner, thus reducing the amount of extractives that enters the pulping and papermaking process. By analysis of the composition of the pressate water from an Impressafiner, Tanase et al. (2010) found that it is mainly resin acids that can be removed. Due to the morphology of wood the fatty acids, steryl esters and triglycerides to a large degree remain in the chips.

The ionisable fatty and resin acids are responsible for the charge and reactivity of the colloidal extractives (Back and Allen 2000). Thus, when prepared as pure dispersions colloidal extractives are electrostatically stabilized (Hiemenz and Rajagopalan 1997; Stenius 2000) by the surface charge created by dissociation of the acid groups. Hence the extractives may be destabilized by addition of simple electrolytes (Allen 1979; Swerin et al. 1993; Sundberg K. et al. 1994).

On the other hand, colloidal wood resin released from TMP into process water is also sterically stabilized by soluble polymers originating mainly from wood that adsorb on the resin particles, (Sundberg 1995; Pelton et al. 1980; Swerin et al. 1993). Steric stabilization of colloidal wood resin is strongest in process waters from unbleached TMP and is reduced if the process water is treated with alkali, making the colloids attach more easily to surfaces (Holmbom et al. 1995). This steric stabilization of the colloidal extractives inhibits their agglomeration by simple electrolytes. In order to flocculate them effectively in process waters, either organic or inorganic fixation aids are needed (Sundberg A. et al. 1994).

Adding cationic polyelectrolytes to a suspension may introduce attractive forces, such as bridging, or reduce electrostatic repulsion by neutralizing the particle surface charge. In both cases, polyelectrolytes act as flocculants. They can also act as stabilizers, if their adsorption changes the forces between the surfaces to repulsive, such as steric repulsion or electrostatic repulsion due to charge reversal. Thus, the role of polyelectrolyte is a matter of dosage (Stenius 2000).

It is generally assumed that high molar mass and low charge density polymers induce bridging flocculation, while high charge density and low molar mass polymers flocculate by charge neutralization (Swerin and Ödberg 1997; Stenius 2000).

Factors that affect colloidal stability of the resin are pH, electrolyte concentration, temperature, viscosity and also the chemical composition of the extractives (Allen 1979). The pH affects the liberation of wood resin, as the solubility of the resin and fatty acids increases with increasing pH (Ekman et al. 1990; Sundberg A. et al. 2009). Käyhkö (2002) concluded that the liberation of wood extractives increased by 10-20% upon raising the pH level from 5 to 8.

The objective of the study reported in this paper was to obtain a better understanding of the effects of cationic polyelectrolytes on the interactions with colloidal extractives in the pressate water from an Impressafiner. The colloidal stability and flocculation (kinetics, creaming and sedimentation layer thickness) of the extractives in the pressate water under different conditions were determined by using a Turbiscan Lab instrument. Previously, we have reported on the mass balance and stability in the presence of electrolytes of extractives around the pre-compression equipment, such as an Impressafiner (Tanase et al 2010).

Materials and methods

Process water and extractives

The pressate water samples were collected from the equipment used for pre-compression of chips (Andritz 500 D Impressafiner) in the TMP B line at Holmen Paper Braviken mill, Sweden. Details of the process are given by Tanase et al (2010). The raw material was 100% Norway spruce. The Impressafiner preheats the chips before compressing and delaminating them while squeezing out water. High compression ratio (5:1) inside the Impressafiner produces a quantity of broken fibres and fines. In our experiments the fines and fibres were removed by centrifugation at 1500g, 10min. The supernatant was collected and used for further analysis.

The amount and composition of extractives in the pressate water from Impressafiner was analyzed as soon as possible after sampling by extraction with MTBE and chromatography, using the method described by Örså and Holmbom (1994). Moreover, the amount of carbohydrates was determined using the method described by Chaplin and Kennedy (1986), using an UV-Vis spectrophotometer. The pressate water from Impressafiner (1ml) was mixed with 1 ml phenol solution (5g/100ml) and 5 ml concentrated acid sulphuric (96%). Thereafter, it was allowed to cool down for 10 minutes, mixed well and left for cooling for 30 minutes. The total amount of carbohydrates is determined by measuring the absorbance at 490 nm, using plastic kyvettes.

The concentrations of carbohydrates and different extractives are given in *Table 1*.

Table 1. Concentration of extractives and carbohydrates from Norway spruce in pressate water from Impressafiner

Dissolved and colloidal substances	**Concentration mg/l**
Fatty acids	129
Resin acids	154
Lignans	189
Sterols	27
Steryl esters	54
Triglycerides	61
Carbohydrates	1470

Chemicals

Poly-(N,N-dimethyl-3,4-diethyl-pyrrolidonium chloride), Poly-DADMAC, with high charge density (CD) and low molar mass (M_w) and cationic polyacrylamides, C-PAM, (cationic substituent trimethyl-3-methacrylamidopropyl-ammonium chloride) with high M_w and low CD (Kemira Oyj, Finland), were used to evaluate the effects of the polymers on the stability of colloidal extractives in process water (*Table 2)*. They were used as delivered without further purification. Prior to experiments, solutions of poly-DADMAC (0.3g/l) and C-PAM (0.8g/l) were prepared.

Table 2. Properties of the cationic polymers used, Poly-DADMAC and C-PAM

Substance	M_w 10^6g/mol	CD meq/g	DS* mol-%
Poly-DADMAC	0.17	6.2	100
C-PAM	7	0.3	2

*DS, degree of substitution, is the percentage of monomers carrying a charged group

Experimental methods

Turbidity was measured in Nephelometric Turbidity Units (NTU) as a function of the amount of polymer used for flocculation of extractives. Different concentrations of polymers were added to the suspension of colloidal extractives, mixing 1 min with a magnetic stirrer before centrifugation (1500g, 10 min). The turbidity was measured before centrifugation and also on the supernatant after centrifugation. Note that the turbidity values may increase in some cases upon formation of small, stable aggregates (flocs), but will decrease if flocs are removed by centrifugation. Also, suspensions of extractives that differ in colloidal size distribution will differ in their measured turbidity values at a given resin concentration.

Sedimentation rate was measured with a Turbiscan Lab instrument (FormulAction, L'Union, France). This instrument measures transmission and backscattering of light (λ = 850nm) from both dilute and concentrated dispersions. The principle of this instrument is shown in *Fig 1*. A detection head with two synchronous detectors head scans the entire length of the sample (about 65 mm) in a flat-bottomed cylindrical cell, acquiring transmission and backscattering data every 40 µm at a rate of maximum 1625 scan/min. For details, see Mengual et al. (1999).

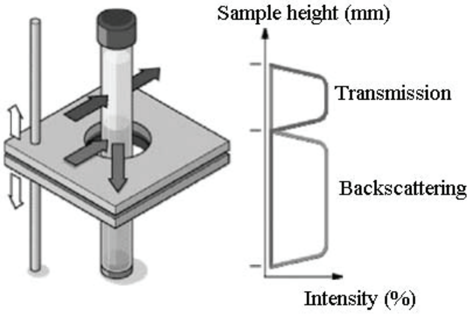

Fig 1. Turbiscan Lab measurement principle. Transmission and backscattering from a sample which has partially sedimented (Mengual et al, 1999).

Particle size determination was performed with a Malvern Mastersizer (Malvern Instruments Ltd, UK) on the Impressafiner pressate water. Impressafiner pressate water was filtered on a wire to remove the large particles. 800 ml suspensions of 600 ml distilled water and 200 ml Impressafiner pressate water mixed with polymers were prepared at room temperature and the particle size distribution was measured. During measurement flocs were suspended by gentle stirring in the measurement cell to avoid settling. The concentrations of polymers used were the optimum polymer dosage (polymer concentration to obtained maximum flocculation).

Electrophoretic mobility was measured using a Malvern Zetasizer Nano ZS instrument (Malvern Instruments, UK) at different concentrations of polymers. A suspension consisting of 10 ml Impressafiner pressate water and 10 ml solution of polymers in distillate water was mixed for 1 min with a magnetic stirrer at 400 rpm, room temperature after which the mobility was measured.

pH of the samples was measured as a function of addition of polymers. The measured pH was in the range of 5.1-5.5. The native pH of the Impressafiner pressate water was 5.5.

Results

Turbidity and electrophoretic mobility

The results from turbidity measurements (*Figs 2* and *3*) show that by using different cationic polymers (C-PAM, poly-DADMAC or a combination of polymers) it was possible to flocculate the colloidal wood extractives present in the pressate water from Impressafiner.

Figs 2 and *3* show the turbidity and the electrophoretic mobility of the resin particles after addition of poly-DADMAC. The negative value of the mobility increased to zero when 0.8-1.0 mg/l poly-DADMAC was added and remained zero at higher concentrations. The charge density of the poly-DADMAC is high and its molar mass is comparatively low. The polymer is therefore expected to adsorb in a flat conformation, binding stoichiometrically to the anionic groups on the resin particles. The electrophoretic mobility confirmed this adsorption mechanism.

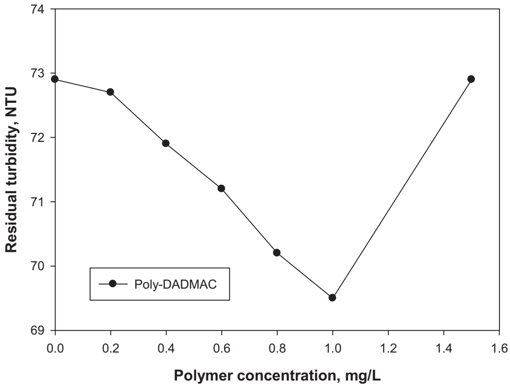

Fig 2. Residual turbidity measured after addition of poly-DADMAC to pressate water from Impressafiner

Fig 2 also shows that the residual turbidity measured after addition of poly-DADMAC decreased until a minimum was reached at the polymer concentration of 0.67 mg/mg (1mg/l). This polymer concentration yields maximum flocculation and is denoted optimum polymer dosage. At the optimum polymer dosage the colloidal extractives are aggregated and sediment during centrifugation.

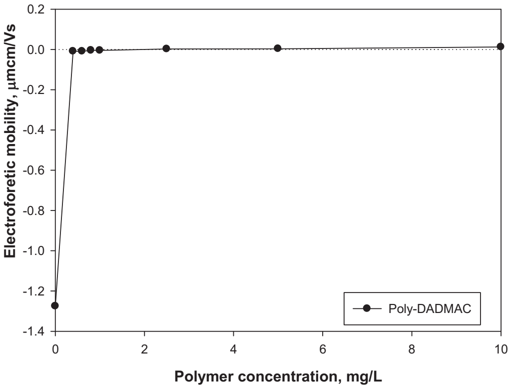

Fig 3. Electrophoretic mobility measured after addition of poly-DADMAC to pressate water from Impressafiner

For poly-DADMAC, optimum dosage correlated with the lowest concentration at which electrophoretic mobility was zero. Thus, it is obvious that poly-DADMAC flocculates the colloids by charge neutralization. At higher concentrations of Poly-DADMAC the residual turbidity increased, indicating restabilization of some particles. A possible explanation for this restabilization is that the particles are rendered positive by adsorption of excess Poly-DADMAC. However, the mean value of the electrophoretic mobility remained very low, so it appears that some other stabilisation mechanism is also of importance.

Figs 4 and 5 show the turbidity and electrophoretic mobility after addition of C-PAM and C-PAM in combination with poly-DADMAC (1:1 mass ratio). As expected, due to the low charge density of C-PAM, a higher concentration of C-PAM (0.25 mg/mg or 50 mg/l) than that of poly-DADMAC was required to reach zero electrophoretic mobility. Also, the mobility became positive at higher concentration, i.e. excess charge was adsorbed because the high molar mass C-PAM formed loops and tails with cationic groups that did not bind directly to anionic groups on the particles. The residual turbidity measured after addition of polymer decreased with increasing polymer concentration until a broad minimum was reached in the range of 0.3-0.4 mg/mg (20-30 mg/l). This behaviour is typical for polymers that flocculate by bridging.

C-PAM added in combination with poly-DADMAC (1:1 mass ratio) resulted in zero electrophoretic mobility at a total concentration of 0.2 mg/mg (20 mg/l). The residual turbidity decreased with increasing the polymer dosage until a minimum was reached at polymer concentration of 0.5 mg/mg (15 mg/l) *figs 4 and 5.*

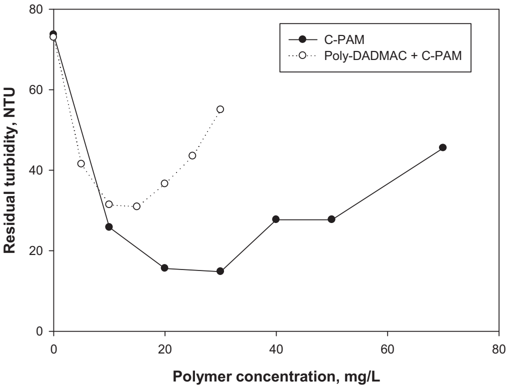

Fig 4. Residual turbidity of Impressafiner pressate water after addition of C-PAM and a combination of C-PAM and poly-DADMAC

As with C-PAM alone, the electrophoretic mobility turned positive and turbidity increased at higher polymer concentrations, i.e. the colloidal extractives were stabilized by adsorption of excess polymer and were no longer removed during centrifugation.

It is well known that pH of the water samples affects the stability of colloidal extractives (Johnsen et al. 2004; Sundberg et al. 2009). At higher pH level the fatty and resin acids are dissociated and to some extent dissolved. The native pH of the pressate water from Impressafiner was 5.5. Moreover, addition of polymers to the Impressafiner pressate water gives almost no reduction in pH which was found to be in the range of 5.1-5.5.

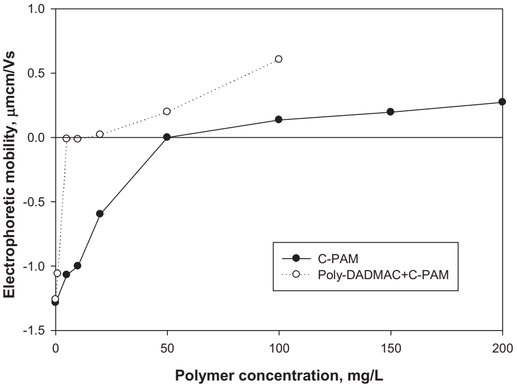

Fig 5. Electrophoretic mobility measured after addition of C-PAM and combination of polymers to the Impressafiner pressate water

Sedimentation

The sedimentation and flocculation efficiency of the colloidal extractives present in pressate water from Impressafiner was measured as a function of the concentrations of cationic polymers used as flocculation agents using a Turbiscan Lab instrument.

To illustrate the performance of the Turbiscan Lab, an example of destabilization of a water suspension depending on its formulation is presented in *fig 6*. The figure shows the initial transmission of Impressafiner pressate water suspension as a function of height of the sample in the Turbiscan test tube for each of the polymers investigated. The concentrations of polymers were chosen to be the optimum polymer dosages. At the beginning of the experiments, an early sedimentation phenomenon gives rise to a very low transmission followed by a sharp increase at the bottom of the cell for all samples. Particle growth in the suspension will be observed as a decrease in transmission, in the middle of the sample.

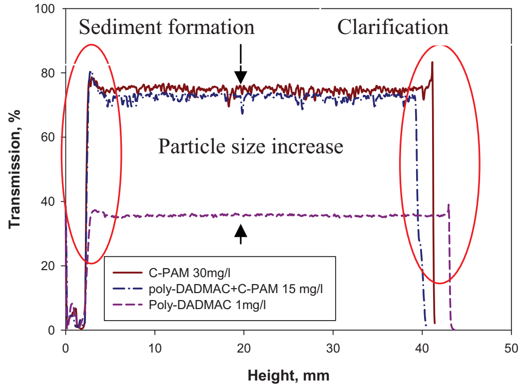

Fig 6. Transmission versus height at time zero for different cationic polymers

Table 3 presents initial transmission and final transmission (2 h after addition of polymer) at different polymer concentrations.

Particle migration leading to sedimentation or creaming phenomena can be characterized by calculation of the migration velocity (*Fig 8*), or of the sediment / cream phase thickness (delta H) (*Fig 7*). The phase thickness is the thickness of the sediment or cream layer in the test tubes (red ovals in *Fig 6*). The migration velocity is the slope of the clarification phase thickness (migration of the particles in the top of the test tubes over time) as a function of time.

Table 3. Transmission as a function of different polymers concentration. T_0 = transmission at time zero, T_{final} = transmission at final time, 2h.

Polymer	**Conc.** mg/l	T_0 %	T_{final} %
C-PAM	30	70.3	69.9
	40	54.2	55.3
	50	46.6	46.2
Poly-DADMAC	0.8	35.2	35.8
	1	33.7	34.1
	1.5	34.8	35.6
Poly-DADMAC + C-PAM	10	62.1	63.0
	15	67.1	67.1

Figs 7 and *8* summarize the Turbiscan results in terms of sediment layer thickness and migration velocity. The highest sediment layer was obtained with C-PAM (30 mg/l), while poly-DADMAC (1 mg/l) gives a more compact sediment layer. Combination of the polymers gives a layer of intermediate thickness.

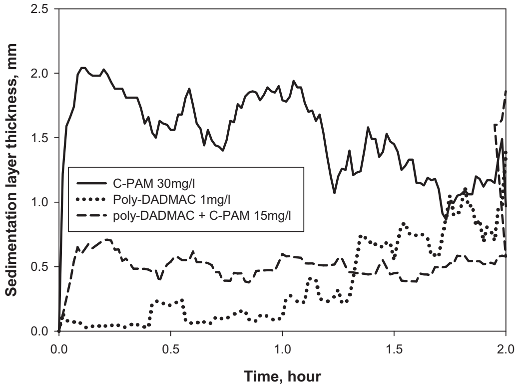

Fig 7. Phase thickness of sediment layer measured with Turbiscan instrument for Impressafiner pressate water after addition of different polymers

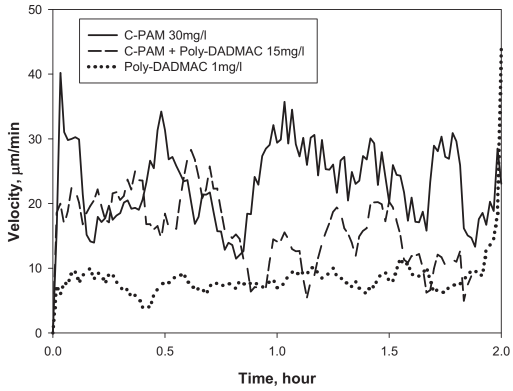

Fig 8. Migration velocity measured with Turbiscan instrument for Impressafiner pressate water after addition of different polymers

These results further confirm that poly-DADMAC flocculates the colloid by charge neutralization, which is expected to give rise to compact, small flocs. Such flocs, as shown by the migration velocity, sediment slowly, forming compact sediments that contain little water. On the other hand, the high sediment volume obtained with C-PAM confirms that this polymer flocculates by bridging, which give rise to rapidly sedimenting, large flocs and sediments containing a lot of water. Combination of the polymers seems to result in relatively compact flocs that nevertheless sediment faster than those formed by poly-DADMAC alone. From a practical point of view, this combination will be advantageous as it combines rapid flocculation and sedimentation with the formation of flocs that do not bind a lot of water.

Table 3 shows that there were insignificant changes in transmission over time which implies that the polymer absorption and particle destabilization occurred very rapidly, in the first minutes of measurements.

Particle size distribution

Measurements of particle size distribution of the pressate water from Impressafiner after addition of polymers yielded additional information on the way the polyelectrolytes flocculated the colloidal extractives, *Fig 9*.

C-PAM (20 mg/l) formed the largest aggregates. Combination of the polymers, poly-DADMAC+C-PAM, (mass ratio 1:1, polymer concentration 20 mg/l) induced formation of relatively large flocs, but much smaller than C-PAM alone. On the other hand, when poly-DADMAC (1 mg/l) was added the flocs formed were small and more compact. The results are in full agreement with the conclusions with regard to flocculation mechanism drawn from the Turbiscan results.

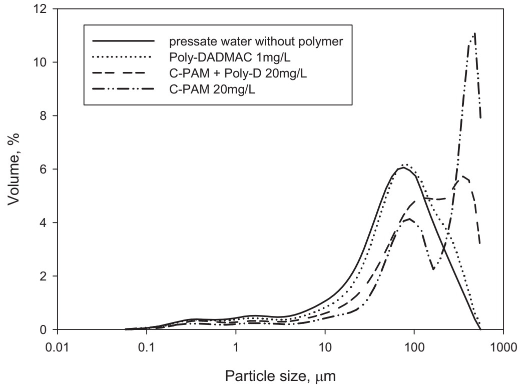

Fig 9. The size distribution of colloidal particles formed by extractives in pressate water from Impressafiner

Discussion

Turbidity and electrophoretic mobility results (*Figs 2 and 3*) showed that addition of excess of polymers may lead to stabilization rather that flocculation. Since restabilization of the water suspension occur at an excess of added polymer, a clearly defined optimum polymer dosage occurs (i.e. the polymer dosage needed to obtain the maximum flocculation).

Moreover, the results show that the polymer properties affect the mechanism behind flocculation and floc strength. Because of its low molar mass and high charge density, poly-DADMAC will adsorb on colloidal particles in a flat conformation, flocculating them by neutralizing their charge as showed by measurements of electrophoretic mobility and residual turbidity (*Figs 2, 3*). In this case the optimum polymer dosage corresponds to the smallest dose which gave zero electrophoretic mobility. Flocs formed by poly-DADMAC are small, sediment slowly and are sensitive to polymer dosage.

A low charge density and high molar mass C-PAM is able to bind more particles together from a larger distance giving rise to bridging flocculation mechanism. These flocs are large and sediment rapidly but the flocs can be disintegrated by too strong mixing. For C-PAM the optimum polymer dosage does not coincide with zero electrophoretic mobility because the flocculation mechanism, bridging flocculation does not require charge neutralisation.

The combination of the polymers (poly-DADMAC + C-PAM) seemed to give the strongest and the most stable aggregates. Tentatively, the following mechanism can be suggested. The highly charged poly-DADMAC adsorbs as comparatively flat patches at the surface of the colloidal particles. The patches of cationic poly-DADMAC prevent the tails of C-PAM from eventually lying down on the surfaces, thus enhancing and preserving the capacity of C-PAM to act as a bridging flocculant by attaching to other colloidal particles even if some flocs are disintegrated by stirring (Swerin et al. 1996).

The floc sizes at the optimum polymer dosage could be evaluated by sedimentation rates and particle size distributions. They largely confirm that C-PAM and combination of the polymers give rise to the largest flocs (bridging flocculation mechanism), while poly-DADMAC induce charge neutralization mechanism (smaller and more compact flocs).

Bridging is the most effective flocculation mechanism, but mixing has to be controlled because flocs may be redispersed by mixing, leading to restabilization or reflocculation to flocs of different size and strength (Stenius 2000).

The results show that different cationic polymers can be used as efficient flocculant of extractives present in the pressate water from the Impressafiner. The results suggest that a flotation technique e.g. Dissolved Air Flotation (DAF) may be a convenient method to remove extractives from the Impressafiner pressate water. A study of this possibility will be presented in a following paper.

Conclusions

Our results show that different cationic polymers (C-PAM, poly-DADMAC and combination of the polymers) can be used to flocculate extractives present in the Impressafiner pressate water. Moreover, the results show that the polymer properties affect the mechanism behind flocculation and floc strength.

Clear differences were observed between a polymer with high charge density and low molar mass (Poly-DADMAC) and a polymer with low charge density and high molar mass (C-PAM). Poly-DADMAC flocculates by charge neutralization while C-PAM flocculates by bridging.

The polymer that flocculated by charge neutralisation yielded compact, slowly sedimenting flocs, indicating that the polymer was adsorbed in a flat layer on the particle surface without charge reversal at high polymer concentrations. The bridging polymer on adsorption formed loops and tails extending into the liquid phase. Flocculation yielded large, rapidly sedimenting flocs, and a sediment with high water content.

Combining a low molar mass, high charge density (poly-DADMAC) cationic polymer with a high molar mass, low charge density polymer (C-PAM) resulted in relatively compact flocs that nevertheless sedimented rapidly. Charge reversal occurred at high polymer concentrations.

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Paper III

Opedal Tanase M., Stenius P., Gregersen Ø.,
Johansson L. and Hill J. (2011):
Removal of dissolved and colloidal substances from TMP process
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REMOVAL OF DISSOLVED AND COLLOIDAL SUBSTANCES FROM TMP PROCESS WATER USING DISSOLVED AIR FLOTATION. LABORATORY TESTS

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KEYWORDS: Thermomechanical pulping, extractives, Dissolved Air flotation, flocculation, turbidity

SUMMARY: This paper reports on an evaluation of the removal of flocculated extractives using Dissolved air flotation (DAF) from two thermomechanical pulp (TMP) process streams: pressate water from Impressafiner and process water from chip washer. The efficiency of the DAF was evaluated by measuring the turbidity, chemical oxygen demand (COD) and the amount of extractives, carbohydrates and lignin present in the subnatant. The laboratory tests showed that a combination of the polymers (C-PAM + Poly-DADMAC, mass ratio 1:1) gave the best results, both in the flocculation of colloidal extractives present in the process water and in the efficiency after DAF. Moreover, by using DAF the flocculated extractives could be removed with a removal efficiency of 80-90%.

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Thermomechanical pulping generates wood-derived compounds that are dissolved or dispersed in the process water, such as carbohydrates, low-molar mass organic acids, pectic acids, lignans, lipophilic extractives and lignin related substances (Thornton 1993). The dissolved and colloidal organic substances in circulating waters in TMP mills have been well characterized in several studies, since many of them are detrimental both to paper quality and the process efficiency (Sjöström 1990; Nylund et al. 1993; Thornton 1993; Sundberg A. et al 1993; Sihvonen et al.1998; Back and Allen 2000). Increasing closure of process water circuits in paper mill results in accumulation of these substances, which may lead to formation of deposits, foaming, runnability problems and uneven paper quality (“pitch problems"). Therefore, removal of detrimental substances from process water is of great importance for the improvement of paper machine efficiency. In some cases the total energy consumption during subsequent refining can also be reduced (Sabourin 2000; Sabourin et al. 2002).

In process water, wood extractives are present in different physical forms, such as colloidal droplets with negative charge, dissolved or attached to the fines and fibres (Allen 1975; Swerin et al.1993; Sundberg et al. 1996; Richardson and Grubb 2004). It is therefore important to know in which form they exist in order to control their behavior and to find the optimum treatment of the process water. Moreover, extractives (e.g. resin acids) are generally regarded as the main acute toxicity contributors in TMP effluents (Magnus et al. 2000). Therefore it is important that small process streams with high concentration of organic substances are treated before they reach toxic levels in the process water or before the water is sent to the effluent plant.

Two ways used to prevent detrimental substances from circulating in the white water system and reduce deposition problems are attachment to the paper web with chemicals (retention aids, e.g. organic polymers) or adsorption onto special pigments (Wågberg and Ödberg 1991; Sundberg A. et al. 1993). It has been shown that highly cationic, but fairly low-molecular organic polymers attach colloidal pitch droplets to fibres, thus carrying the pitch out with the paper in a less detrimental form. The drawback of using retention aids is that high amount of wood extractives retained in the paper will affect the paper properties (Holmbom and Sundberg A., 2003).

Washing mechanical pulp is a good way to remove extractives (Käyhkö 2002), but fibre recovery is needed and hence, becomes less efficient. Thus, in order to achieve high closure, it becomes necessary to eliminate harmful substances or at least to decrease their negative effect as early as possible in the process. Sabourin (2000) and Sabourin et al. (2002) show that using equipment for compressive pre-treatment of the chips, such as an Impressafiner, the chips are to some degree defibrated but the fibres are still intact. Moreover, using such equipment extractives can be removed from the wood chips before refining, thus reducing the amount of extractives that enter the pulping and papermaking processes (Sabourin et al. 2002; Tanase et al. 2010a). The extractives removed from the Impressafiner will enrich in the process water. Treatment of this water is important in order to avoid that the extractives enter the effluent treatment or reach undesirable levels in the process water.

Dissolved Air Flotation, DAF, is a process that can remove problematic components by attaching them to bubbles generated when a pressurized solution of air in water is released into the flotation cell. Flotation generally does not efficiently remove particles smaller than a few µm, and thus particles smaller than that have to be flocculated before flotation.

Colloidal extractives can be flocculated with cationic polymers. The flocs then attach to the bubbles, which rise to the surface, taking with them much of the undesirable components of the process water and forming a layer of sludge at the top. Richardson and Grubb (2004) investigated the removal of extractives from thermomechanical process water by DAF. The waters studied were cloudy white water (derived primarily from the disk filter that concentrates pulp after the cleaners) and reject filtrate (derived from concentrating the fibre prior to reject refining). It was found that 80-90% of the fibre-bound and colloidal extractives could be removed in this way. DAF has also been beneficially applied for removal of extractives in a eucalyptus kraft mill in order to control pitch deposition (Negro et al. 2005) and for removal of detrimental substances from peroxide-bleached thermomechanical pulp water (Saarimaa et al. 2006).

Previously (Tanase et al. 2011a) we have shown that compressive pre-treatment (i.e. an Impressafiner) disperses extractives into the process water and that the dispersed particles can be efficiently flocculated by cationic polymers. Two cationic polymers were investigated, a cationically modified poly(acrylamide) (C-PAM), and poly(dimethyldiallylammonium) chloride (Poly-DADMAC). A combination of these polymers was also used.

This work described in this report focused on two thermomechanical process water streams (TMP) with high concentrations of extractives: Impressafiner pressate water and process water from a chip washer. The aim was to clarify to what extent flocculated lipophilic extractives can be removed from such waters using DAF. In a follow-up pilot trial in a paper mill the potential benefits of DAF in mill scale were assessed. The results from this trial will be described in a forthcoming paper.

Materials and methods

Process water

Two different mill process water samples were collected. One was taken from the equipment (Andritz 500 D Impressafiner) used for pre-compression of Norway spruce chips in the TMP B line at Holmen Paper Braviken mill, Sweden. The other was from a chip washer at Norske Skog Skogn mill, Norway. The samples from the Impressafiner were transported to the laboratory at NTNU where they were stored in a frozen state until subjected to testing and treatment. After melting, the Impressafiner pressate water was filtered on a metal wire (1mm mesh) to remove large particles and used directly for DAF experiments. This implies that small fibre fragments may have been present in the water, but a general observation was that there were very few fibres in water from the Impressafiner. The process water samples from the chip washer were used fresh, without freezing.

Chemicals

Solutions of Poly-(N-N-dimethyldiallyl-3-4-ethylen-pyrrolidonium)chloride, Poly-DADMAC, i.e. a polymer with high charge density (*CD*) and low molar mass (M_w) and a cationically modified polyacrylamide, poly(trimethyl(3-methacrylamidopropyl)-ammonium)chloride, C-PAM, i.e. a polymer with high M_w and low *CD* (Kemira Oyj, Finland), were used (*Table 1*). They were used as delivered without further purification.

Table 1. Properties of the cationic polymers used, Poly-DADMAC and C-PAM. *DS* is the degree of substitution, i.e. the fraction of monomers in the polymer that carries a cationic group

Substance	M_w 10^6g/mol	CD meq/g	DS* mol-%
Poly-DADMAC	0.17	6.2	100
C-PAM	7.0	0.3	2.0

Experimental methods

Polymer addition

Electrophoretic mobility measurements of both water suspensions have been used for assessing the polymers concentrations to be used in our experiments (Tanase et al. 2011a). Different amounts of polymers was necessary to reach zero electrophoretic mobility, such as: poly-DADMAC 1 mg/l, C-PAM 50 mg/l and combination of the polymers (Poly-DADMAC + C-PAM, 1:1 mass ratio) 20 mg/l. Thus the concentrations of the polymers used in our laboratory DAF tests were chosen to be concentrations around the isoelectric point.

Various amounts of C-PAM (0-120 mg/l), Poly-DADMAC (0-100 mg/l) and combination of the polymers (0-90 mg/l) were added to the Impressafiner pressate water during slow agitation (1 min, 100 rpm) in order to promote the interaction of the flocculants with dispersed organic substances and to facilitate the growth of the flocs. When using a combination of the polymers, the Poly-DADMAC was added first, with an interval of 10 sec before adding the C-PAM in order to allow the adsorption of Poly-DADMAC on the particle surface. The concentrations of the polymers added to the chip washer water were in the same range C-PAM (0-300 mg/l), Poly-DADMAC (0-120 mg/l) and combination of the polymers (0-90 mg/l).

The **flotation** experiments were performed using a laboratory scale DAF unit (*fig. 1*) at room temperature and at the native pH of the process water (pH 5.5). The volume of sample in the cell was 1 l and the height of the column of process water was 41 cm. Water from the Impressafiner was first filtered on a metal wire (1mm mesh) to remove large particles and then mixed with different concentrations of polymers. Solutions of Poly-DADMAC (0.3 g/l) and C-PAM (0.8 g/l) were prepared.

Air-saturated water (5 bar, 23^{o}C) was injected at the bottom of the flotation cell. A constant time, 7 min was allowed to pass after addition of flocculants before the air-water mixture was released into the flotation cell. Flocs formed by the polymers and extractives attached to the bubbles and rose up to the surface. After 10 min, a sample of the subnatant was taken and subjected to analysis of turbidity, chemical oxygen demand (COD) and lignin content as well as content and composition of carbohydrates and extractives.

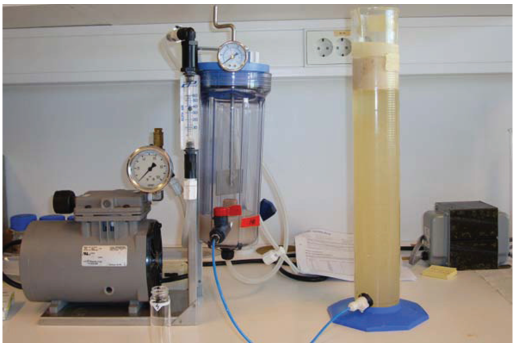


Fig 1. Dissolved Air Flotation unit

Turbidity was measured in Nephelometric Turbidity units (NTU), using a laboratory turbidimeter (Hach Model 2100AN). The turbidity of the subnatant after DAF, was measured as a function of the amount of cationic polymer added to the both processes waters.

The **Chemical Oxygen Demand**, COD, was measured according to the Dr. Lange method (ISO 6060-1989).

The residual **lignin** was be determined by extracting the lignans from the process water with methyl tert-butyl ether (MTBE) and measuring the absorbance at 280 nm using a UV-Vis spectrophotometer (Örså and Holmbom 1994).

The amount of **carbohydrates** was determined using the methods described by Chaplin and Kennedy (1986). The process water from both Impressafiner and Chip washer (1 ml) was mixed with 1 ml phenol solution (5 g / 100 ml) and 5 ml concentrated sulphuric acid (96%). Thereafter, it was allowed to cool down for 10 minutes, mixed well and left for cooling for 30 minutes. The total amount of carbohydrates (see Table 2) was determined by measuring the absorbance at 490 nm, using plastic cuvettes.

The amount and composition of **extractives** in the process water was analyzed as soon as possible after sampling by extraction with MTBE followed by gas chromatographic analysis, using the method described by Örså and Holmbom (1994). The amounts are given in *Table 2*.

Table 2. Concentration of extractives, carbohydrates and lignans in process water from the Impressafiner and chip washer

Substances	Impressafiner pressate water	Chip washer
	Concentration, mg/l	Concentration, mg/l
Fatty acids	112	86
Resin acids	299	119
Lignans	195	231
Sterols	29	33
Steryl esters	63	91
Triglycerides	108	107
Total extractives	806	667
Carbohydrates	1616	2785

Results

Figs 2-10 describe flotation efficiency in terms of the amount of polymer added to both processes waters. The actual amount of polymer added in mg/l varies between samples.

The turbidity measurements showed that the turbidity decreased with increasing polymer dosage, indicating that the air bubbles after flocculation of the particles effectively lifted them to the surface. *Figs 2* and *3* summarize the flotation efficiency in terms of reduction of turbidity in the subnatant after flotation for both Impressafiner pressate water and process water from chip washer.

When Poly-DADMAC was used as the flocculation agent the turbidity of Impressafiner pressate water was reduced by 83% after DAF at a polymer dosage of 100 mg/l. The turbidity of chip washer water was reduced by 82% at a polymer dosage of 120 mg/l.

On the other hand, using cationic polyacrylamide (C-PAM) as flocculation agent, DAF reduced the turbidity of both waters by 90% at the same polymer concentration 120 mg/l. When more C-PAM was added to the chip washer water, the turbidity was finally reduced by 98% after DAF at a polymer concentration of 300 mg/l, see *fig. 3.* C-PAM in combination with Poly-DADMAC (1:1 mass ratio) gave the best reduction in turbidity after DAF (95%) at a polymer concentration of 70 mg/l, for both processes waters.

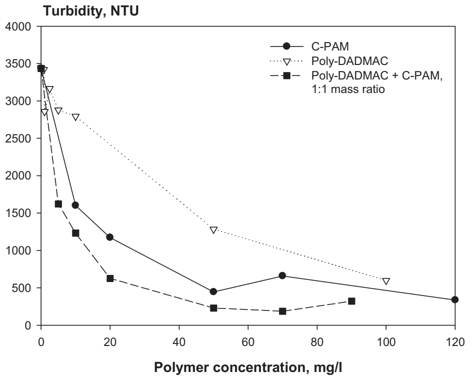


Fig 2. Turbidity of Impressafiner pressate water after DAF

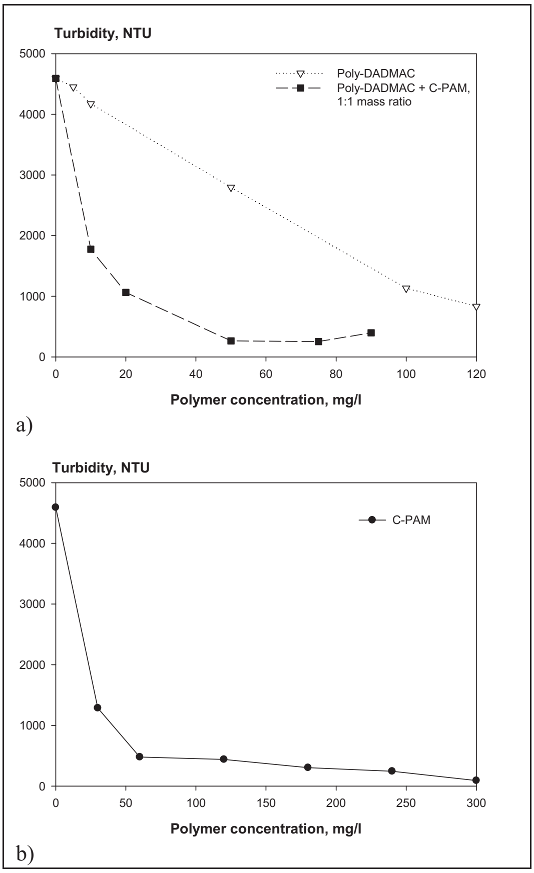


Fig 3. Turbidity of chip washer water after DAF, a) Poly-DADMAC and combination of the polymers; b) C-PAM

Figs 4 and *5* summarize the flotation efficiency in terms of reduction of extractives in the subnatant after flotation, for both Impressafiner pressate water and process water from chip washer. Adding Poly-DADMAC alone reduced the total amount of lipophilic extractives in Impressafiner water by 26% at a dosage 1 mg/l. By adding more polymer did not significantly change this amount (*Fig 4*). At the polymer dosage of 10 mg/l the amount of lipophilic extractives in chip washer water was reduced by 15%, but adding more polymer reduced the amount continuously to reach a value of 65% at a polymer dose of 120 mg/l, *see fig 5*.

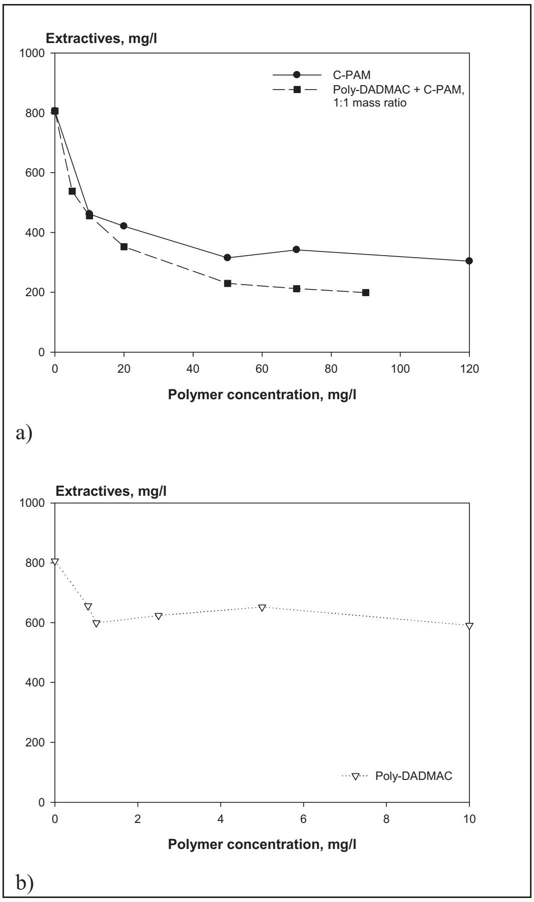
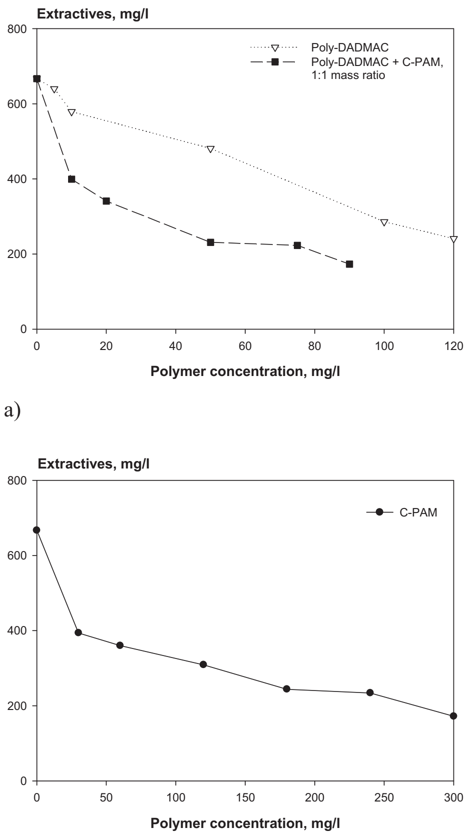


Fig 4. The amount of lipophilic extractives in Impressafiner process water after DAF a) C-PAM and combination of the polymers; b) Poly-DADMAC

When C-PAM was used as flocculation agent for Impressafiner pressate water the total amount of lipophilic extractives was reduced by 61% at a polymer dosage of 50 mg/l. Higher concentration of C-PAM did not result in further reduction. When C-PAM was added to the chip washer water reduced the total amount of lipophilic extractives by 55% at a polymer concentration of 120 mg/l. By increasing the polymer concentration in the process water from chip washer the total amount of lipophilic extractives was reduces by 74% at a polymer concentration of 300 mg/l.

C-PAM in combination with Poly-DADMAC (1:1 mass ratio) gave the best reduction in total amount of lipophilic extractives. Addition of 90 mg/l removed 75% of the extractives from both Impressafiner pressate water chip washer water. The combination of polymers also seemed to give the strongest and most stable aggregates.



a)

b)

Fig 5. The amount of lipophilic extractives in chip washer water after DAF, a) Poly-DADMAC and combination of the polymers; b) C-PAM

Figs 6 and *7* summarize the flotation efficiency in terms of reduction of carbohydrates in the subnatant after DAF. Using Poly-DADMAC alone reduced the amount of carbohydrates in Impressafiner water by 50%, at a polymer dosage of 100 mg/l and in chip washer water by 63% at a polymer dose of 120 mg/l. The lowest reduction of carbohydrates was obtained when using C-PAM as flocculation agent. Adding 120 mg/l, C-PAM reduced the amount of carbohydrates in Impressafiner water by 43% and in chip washer water by 41%. Increasing the polymer dose the amount of carbohydrates was reduced by 62%, at a polymer dose of 300 mg/l for process water from chip washer, see *fig. 7*.

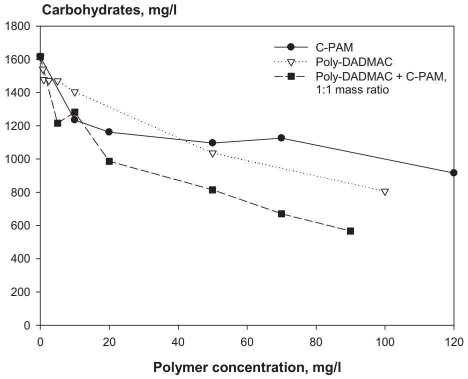
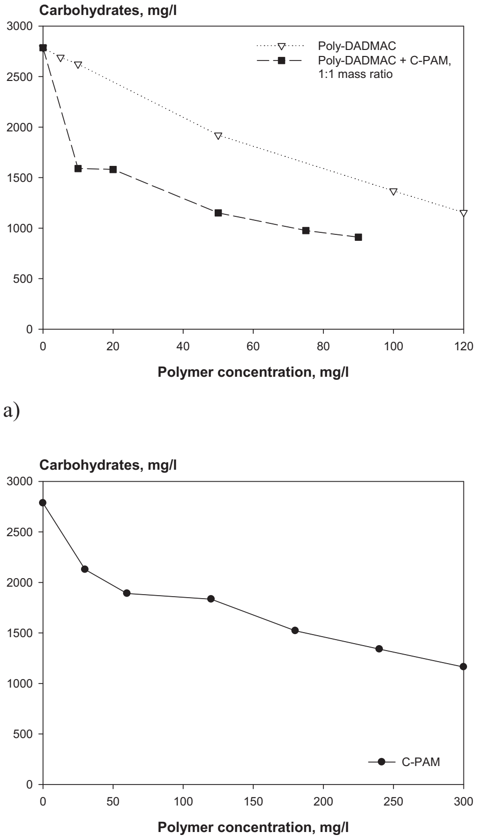


Fig 6. The residual amount of carbohydrates in Impressafiner pressate water after DAF



a)

b)

Fig 7. The residual amount of carbohydrates in chip washer water after DAF a) Poly-DADMAC and combination of the polymers; b) C-PAM

The combination of the polymers (C-PAM + Poly-DADMAC) gave the best removal of carbohydrates from both waters, 65% for Impressafiner pressate water and 71% for process water from chip washer, at the same polymer dosage of 90 mg/l.

The flotation efficiency was also determined by measuring the chemical oxygen demand (COD). The best reduction in COD was obtained with the combination of the polymers (Poly-DADMAC + C-PAM), 71 % for Impressafiner pressate water and 70% for process water from chip washer, observed at the same polymer dose 90 mg/l. When Poly-DADMAC was used alone as flocculation agent the same reduction in COD (67%) was observed at the polymer dose of 100 mg/l for Impressafiner pressate water and at a polymer dose of 120 mg/l for process water from the chip washer. C-PAM alone gave the lowest reduction in COD, 58 % for Impressafiner pressate water and 53% for process water from the chip washer at the same polymer dose 120 mg/l. However, increasing the polymer dose the COD was further reduced by 71% at a polymer dose of 300 mg/l for process water from chip washer.

The residual amount of lignin after flotation was measured for Impressafiner pressate water only (*Fig 8*) and the best reduction obtained was for Poly-DADMAC + C-PAM by 65% at the polymer dose of 90 mg/l, for C-PAM by 45% at polymer dose of 120 mg/l and for Poly-DADMAC by 52% at polymer dose of 100 mg/l.

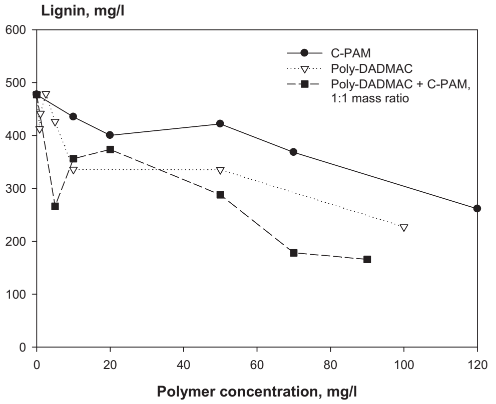


Fig 8. The residual amount of lignin in Impressafiner pressate water after DAF

Particle size distribution

Measurements of particle size distribution of the pressate water from Impressafiner before (*Fig 9*) and after DAF (*Fig 10*) confirm that the polymers used in our study flocculate the lipophilic extractives and that the large flocs are efficiently removed by DAF. The particle size distribution for the chip washer was not measured.

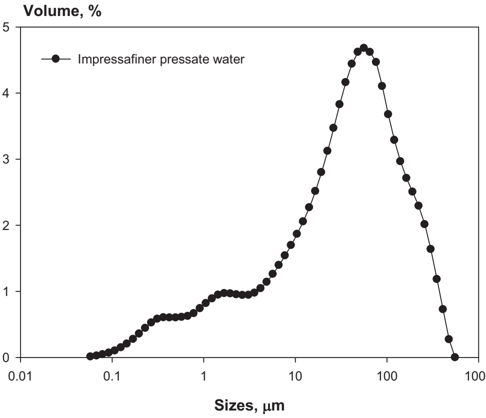


Fig 9. Particle size distribution in Impressafiner pressate water

The results show that large flocs in the range of 100-1000 μm are efficiently removed by DAF. After addition of the flocculating polymers and DAF the particle concentrations were much lower (*Fig 2*) and particle size distribution was dominated by particles in the range 0.1-100 μm that were to small to be removed from the process water by DAF.

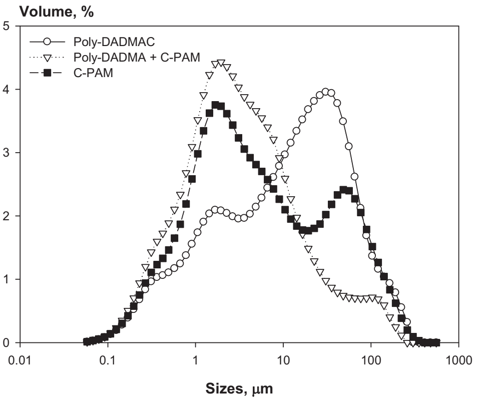


Fig 10. Particle size distribution in Impressafiner pressate water after DAF

Our results, reported in a previous paper (Tanase et al. 2010), show that 30-40% of the extractives in the Impressafiner pressate water were attached to fines and fibres, 40-50% of the extractives were in colloidal form and only 10-13% of extractives were dissolved. After melting, the phase distribution of extractives between colloidal, dissolved and fibre bound did not significantly changed. We have found that 35-40% of the extractives in Impressafiner pressate water were attached to fines and fibres, 40-45% of the extractives were in colloidal form and 13-15% of extractives were dissolved.

For the chip washer water we have found that 35-40% of the extractives were attached to the fines and fibres, 40-45% of the extractives were in colloidal form and 15-20% of extractives were dissolved. The distribution of extractives in different physical forms will affect the efficiency of DAF.

Discussion

The results given in *Table 2* indicate that the main difference between the Impressafiner pressate water and the chip washer water was the concentration of carbohydrates. The concentration of carbohydrates was higher in the chip washer than in the Impressafiner pressate water. This difference in carbohydrates concentration seems to have an effect on the flocculation efficiency of colloidal extractives with polymers. Moreover, it was observed that Impressafiner pressate water contained higher concentration of resin acids compared to process water from the chip washer. The differences in the concentrations of lipophilic extractives (*Table 2)* could be explained by the Impressafiner conditions (i.e. high compression ratio inside the Impressafiner) (Tanase et al. 2010a).

The turbidities (*Figs 2* and *3*) and amounts of extractives (*Figs 4* and *5*) after flotation confirm that the flocculation efficiency of colloidal extractives with polymers was affected by the presence of carbohydrates. A single component system (Poly-DADMAC) showed the lowest removal efficiency. A likely explanation is that the Poly-DADMAC, which is a highly charged polycation, reacts with dissolved carbohydrates and thus is partially consumed before it neutralizes and flocculates the extractives, as has been found in earlier comparisons of polycations with low and high charge density (Ström et al. 1982). Therefore, a higher concentration of Poly-DADMAC was necessary for flocculation of the colloidal extractives. The selectivity of Poly-DADMAC to react first with dissolved carbohydrates has been previously reported in the literature (Sundberg A. et al. 1993). Another possible explanation is that Poly-DADMAC form compact flocs that are too small to be efficiently removed from the process water by flotation.

On the other hand the higher removal efficiency of C-PAM (*Figs 2* and *3*) can be due to the flocculation mechanism. C-PAM induces bridging flocculation mechanism, the flocs are larger and they are not that sensitive to polymer dosage but the flocs may be disintegrated by too strong mixing. For more details, see Tanase et al. 2010b.

The combination of the polymers (Poly-DADMAC+C-PAM) showed the highest removal efficiency for both processes waters (the polymer with the highest ability to remove dissolved and colloidal substances) in terms of total amount of lipophilic extractives in the subnatant after DAF. The high removal efficiency could be explained by a combination of flocculation mechanisms (charge neutralization and bridging flocculation).

The reduction in the COD involves the removal of negatively charged particles present in the TMP process water. Thus, the removal of wood extractives significantly contributes to COD reduction. The remaining COD must be due to dissolved organic substances remaining in the water after flotation. A major portion of the lignans and lignin-related substances remained in the water and gave color to it after flotation. Moreover, the pectic acid and low-molar organic acids such as formic acid, acetic acid were not measured in our water samples. However, it has been shown in the literature that pectic acids, low-molar organic acids, lignans and lignin related substances are the main contributors to the COD (Ekman and Holmbom 1989; Lenes et al. 2001; Holmbom and Sundberg A. 2003).

The differences in the extractives amount and composition found between the two processes waters could be an effect of the storage conditions of the two processes waters. The Impressafiner pressate water was frozen before analyzing and the chip washer water was analyzed fresh, without freezing. It has been reported in the literature that storage in the frozen state gives physicochemical changes in process waters (Willför et al. 2006). However, the fact that Impressafiner pressate water had been frozen, without fractionation does not seem to have resulted in strong differences. The fibre bound, dissolved and colloidal fractions of extractives did not change significantly by freezing.

Particle size distribution results (*Fig 10*) confirmed that by using cationic polymers it was possible to flocculate colloidal extractives present in both Impressafiner pressate water and chip washer. These flocculated particles could be removed from the process water using DAF.

Conclusions

Dissolved Air Flotation seems to be a convenient method to remove extractives from both Impressafiner pressate water and chip washer water. A decrease of COD values, turbidity, content and composition of extractives, carbohydrates and lignin indicates a removal of dissolved and colloidal organic substances.

It appears that the properties of the polymers are important for having an efficient flotation. In flotation the flocs formed by different cationic polymers are subjected to shear and the mechanism that gives large flocs and prevents reduction of the floc size by shear (a combination of a high molecular weight, low charge density polymer with another polymer with lower molecular weight and high charge density) may be the most efficient.

The high charge density polymer (Poly-DADMAC) probably interacted with dissolved carbohydrates present in the process water before acting as a flocculant/neutralizer of particles. Thus it appears that both the amount and the distribution of wood extractives (colloidal, dissolved or attached to fines and fibres) as well as the dissolved carbohydrates in mechanical pulp water will affect the efficiency of cationic polymers and efficiency of DAF respectively.

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Paper IV

Opedal Tanase M., Stenius P., Johansson L., Hill J.
and Sandberg C. (2011):
Removal of dissolved and colloidal substances from compressive
pre-treatment of chips using dissolved air flotation.
Pilot trial, Nordic Pulp and Paper Research Jornal, submitted

REMOVAL OF DISSOLVED AND COLLOIDAL SUBSTANCES IN WATER FROM COMPRESSIVE PRE-TREATMENT OF CHIPS USING DISSOLVED AIR FLOTATION. PILOT TRIAL

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KEYWORDS: Thermomechanical pulping, extractives, Dissolved Air flotation, RT-Impressafiner, Chemical oxygen demand, turbidity

SUMMARY: In this paper, we report on an investigation of the removal of dissolved and colloidal substances in water from compressive pre-treatment of wood chips (Impressafiner pressate water) using a pilot dissolved air flotation (DAF) unit in a paper mill. The flotation efficiency technique was evaluated by measuring turbidity, chemical oxygen demand (COD), and the amounts of extractives, carbohydrates and lignin present in the subnatant before and after flotation. Factors such as pH and temperature of the Impressafiner pressate water affect the efficiency of DAF and are discussed. The results show that the best removal efficiency (up to 76% removal of extractives) was obtained by using a combination of a high molecular weight, low charge density polymer (C-PAM) with a low molecular weight, high charge density polymer (poly-DADMAC + C-PAM) in the mass ratio 1:1.

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In pulp and paper mills, decreasing the fresh water consumption and closing the mill water circulation results in accumulation of dissolved and colloidal substances in the white waters. These substances may cause various problems in the papermaking process, including lower wet strength of the paper web, formation of deposits and corrosion. They also may affect the mechanical and optical properties of the paper, as well as odour and taste in the final product (Allen 1975; Sundberg 1996; Sundberg 2000; Cisneros and Drummond 1995). Deposits are often formed when the colloidal stability is weakened so that the colloidal extractives aggregate. In order to avoid these problems, cationic polymers are added to fibre suspensions with the aim to fix the colloidal substances to the paper by reduced electrostatic repulsion (i.e. by neutralizing the particle charge) or by introduction of attractive forces, such as bridging. In both cases, the polymers act as flocculants. If added in excess, they can also act as stabilizers, if their adsorption changes the forces between the surfaces to repulsive, such as steric or electrostatic repulsion due to charge reversal (Stenius 2000).

In order to reduce the environmental impact of pulp and paper production, small water process streams can be treated to remove both dispersed solid material and dissolved substances before they reach toxic levels in the process water or before the water is sent to the effluent plant. Therefore, it becomes necessary to eliminate harmful substances as early as possible in the beginning of the process or at least to decrease their negative effect. Apart from binding them in to the paper web, dissolved and colloidal substances can be removed from the white water and wastewater by sedimentation, filtration, flotation and reverse osmosis.

Tanase et al. (2010) found that up to 40% of extractives are released when using a compressive pre-treatment of wood chips, such as an Impressafiner. Moreover, also other substances contributing to chemical oxygen demand (COD) are squeezed out. On the other hand, in the COD from the Impressafiner there will be very few fibres.

In this study, a flotation technique (i.e. Dissolved Air Flotation, DAF) was used for removal of flocculated extractives from the Impressafiner pressate water.

In DAF particles in the size range from a few µm upwards are removed by attaching them to micro bubbles that are generated when a pressurized solution of air in water is released into the flotation cell. It is well known that flotation of particles smaller than a few µm is inefficient because hydrodynamic effects on particle collisions decrease the probability of attachment of small particles to much larger bubbles (Han 2001). The size of the colloidal extractives is generally less than a few µm. Thus, they must be flocculated before flotation.

Richardson and Grubb (2004) investigated the removal of extractives from thermomechanical process water by DAF. They found that 80-90% of the fibre-bound and colloidal extractives could be removed in this way. DAF has also been beneficially applied for removal of extractives in a eucalyptus kraft mill in order to control pitch deposition (Negro et al. 2005) and for removal of detrimental substances from peroxide-bleached TMP water (Saarimaa et al. 2006).

In an earlier study (Tanase et al. 2011a), we investigated the flocculation of colloidal extractives present in pressate water from Impressafiner with different cationic polymers (poly-DADMAC, C-PAM and combination of the polymers). It was shown that these polymers efficiently flocculate colloidal extractives present in pressate water from Impressafiner via two different flocculation mechanisms: charge neutralization and bridging flocculation.

Subsequently (Tanase et al. 2011b) we investigated the removal of the flocculated extractives by flotation in a laboratory scale DAF unit. The pressate water samples had been stored in frozen condition before the investigation. It was shown that a combination of the polymers gave the best results, both in the flocculation of colloidal extractives and in the efficiency after DAF. The flocculated extractives could be floated with a removal efficiency of 80%.

This paper reports on an assessment of the potential benefits of DAF in mill scale, using the laboratory results as a background. The removal of flocculated lipophilic extractives from fresh Impressafiner pressate water using a pilot DAF unit in a paper mill was investigated.

Materials and methods

Process water and extractives

The pressate water samples were collected from the equipment used for pre-compression of chips (Andritz 500 D Impressafiner) in the TMP B line at Holmen Paper Braviken mill, Sweden. Details of the process are given by Tanase et al. (2010). In order to simulate a real DAF process conditions, pressate water samples were collected and used directly in the pilot DAF unit at the mill site. The raw material was 100% Norway spruce.

The water used for creation of air bubbles in the DAF tests was pressurized water saturated with air at 6 bar from the deinking plant at the mill. More details are given in *Table 2* and *Table 3*.

Chemicals

Solutions of Poly-(N-N-dimethyldiallyl-3-4-ethylen-pyrrolidonium)chloride, Poly-DADMAC, i.e. a polymer with high charge density (*CD*) and low molar mass (M_w) and cationically modified polyacrylamide, poly-(tri-methyl(3-methacrylamidopropyl)-ammonium)chloride, C-PAM, a polymer with high M_w and low *CD* (Kemira Oyj, Finland), were used (Table 1). The polymers were used as delivered without further purification.

Table 1. Properties of the cationic polymers used, Poly-DADMAC and C-PAM. *DS* is the degree of substitution, i.e. the fraction of monomers in the polymer that carries a cationic group and *CD* is the charge density.

Substance	M_w 10^6 g/mol	*CD* meq/g	*DS* %
Poly-DADMAC	0.17	6.2	100
C-PAM	7.0	0.3	2.0

Experimental methods

Polymer addition

Flocculation with single polymer (Poly-DADMAC, C-PAM) and a mixture of the polymers (Poly-DADMAC + C-PAM, 1:1 mass ratio) was studied.

The concentrations of the polymers necessary to reach zero electrophoretic mobility (isoelectric point) were determined in previous laboratory experiments (Tanase et al. 2011b). They were: poly-DADMAC 1 mg/l, C-PAM 50 mg/l and combination of the polymers (Poly-DADMAC + C-PAM, 1:1 mass ratio) 20 mg/l. The concentrations of the polymers used in the pilot DAF trial were chosen to be the concentrations around these isoelectric points.

Prior to experiments, solutions of Poly-DADMAC (0.3 g/l) and C-PAM (0.8 g/l) were prepared. Appropriate amounts of C-PAM, Poly-DADMAC and the combined polymers were added to pressate water during rapid agitation (1 min), in order to promote the interaction of the flocculants with dispersed organic substances and to facilitate the growth of the flocs. In the case of combination of the polymers (C-PAM + Poly-DADMAC), the Poly-DADMAC was added first with a gap of 10 sec before adding the C-PAM in order to allow the adsorption of Poly-DADMAC on the particle surface.

Dissolved air flotation (DAF) tests were performed in a pilot flotation unit (*fig. 1*) at 70°C and at pH 6.6 -7.1. Process water from Impressafiner was filtered on a plastic wire to remove large particles and mixed with different concentrations of polymers. The DAF cell was filled with 10 L sample.

Air-saturated water (temperature 70°C, pH 7.1) was mixed with flocculated Impressafiner pressate water and injected in the middle of the flotation cell in a continuous flow, 2 L/min (1/3 is pressurised water and 2/3 is mixture of Impressafiner pressate water and chemicals). The pressure used in our experiments was 6 bar. Flocs formed by the polymers and extractives attached to the bubbles and rose up to the surface. The subnatant was subjected to analysis of turbidity, chemical oxygen demand (COD) and lignin as well as content of carbohydrates and extractives.

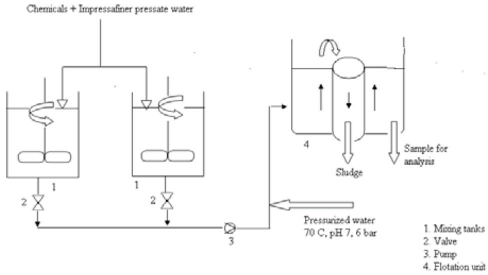

Fig 1. Scheme of the pilot dissolved air flotation unit

Turbidity was measured in Nephelometric Turbidity units (NTU), using a laboratory turbidimeter (Hach Model 2100AN). The turbidity of the subnatant after DAF, was measured as a function of the amount of cationic polymer added to the Impressafiner pressate water (1500 g, 10min).

The Chemical Oxygen Demand, COD, was measured according to the Dr. Lange method (ISO 6060-1989).

The residual **lignin** was be determined by extracting the lignans from the process water with methyl tert-butyl ether (MTBE) (Örså and Holmbom 1994) and measuring the absorbance at 280 nm using a UV-Vis spectrophotometer.

The amount of **carbohydrates** was determined using the methods described by Chaplin and Kennedy (1986). 1 ml of the water to be analysed was mixed with 1 ml phenol solution (5 g/100 ml) and 5 ml concentrated sulphuric acid (96%). Thereafter, it was allowed to cool down for 10 minutes, mixed well and left for cooling for 30 minutes. The total amount of carbohydrates (see *Table* 3) was determined by measuring the absorbance at 490 nm, using plastic cuvettes.

The amount and composition of extractives was analyzed by extraction of the process water with methyl tert-butyl ether (MTBE), using the method described by Örså and Holmbom (1994). The amounts are given in Table 3.

The total amount of extractives in the chips that enter the Impressafiner was calculated by measuring the water flows around the Impressafiner. For more details see Tanase et al. 2010.

The resin acid, triglycerides and fatty acid components of the extractives were measured as total, colloidal and dissolved form. The dissolved and colloidal fraction was isolated by centrifuging the total sample at 500g for 30 min. The colloidal fraction was then removed by ultrafiltration using an Amicon cell with a 0.1µm filter. Based on this procedure the material in the pressate water could thus be classified as fibre bound (i.e., removed by centrifugation, total – dissolved - colloidal), colloidal (removed by centrifugation and filtration, i.e. total-dissolved) and dissolved (remaining after filtration through 0.1 µm filter).

Results

Composition of pressate and pressurized water

The characteristics of the Impressafiner pressate water and pressurized water used in the pilot DAF trial is shown in *Table 2*. The classification and composition of the material in the pressate water are given in *Table 3*.

Table 2. Characterization of the Impressafiner pressate water and pressurized water (initial)

	Impressafiner pressate water	**Pressurized water**
pH	6.6	7.1
Residual turbidity, NTU	711	20
COD, mg/L	6050	2383
Lignin, mg/L	582	352

Table 3. Concentrations of extractives, lignans and carbohydrates in process water from Impressafiner and in the pressurized water used in flotation.

	Impressafiner pressate water				**Press-urized water** mg/l
	Before cenrif. mg/l	After centrif. mg/l	After ultrafiltr. mg/l	*As colloid mg/l	
Fatty acids	56	35	17	18	16
Resin acid	204	93	18	75	19
Lignans	143	149	153	-	78
Sterols	20	17	18	-	8
Steryl ester	44	25	11	14	8
Triglycer.	48	21	0	21	0
Carbohydr.	1434				554

* As colloidal is the difference between after centrifugation and after ultrafiltration.

It is noteworthy that the concentrations of fatty acids, esters and resin acids were considerably reduced already by centrifugation at speeds that will not remove colloidal material. Obviously part of these compounds were either dispersed as relatively large particles or, as is more likely, were bound to fibre fragments that were removed in the centrifugation. In the discussion below, this fraction will be denoted as fibre bound. Within experimental accuracy, no lignans or sterols were removed by centrifugation or filtration. The triglycerides were completely insoluble in water and were released from the chips either bound to fibre fragments or as colloidal particles.

The composition of pressurized water is given in *Table 3.* The water contained some extractives, carbohydrates and lignans, but the concentrations were much smaller than those in the water from the Impressafiner.

Dissolved air flotation

Figs. 2-6 describe flotation efficiency as a function of the amount of polymer added to the pressate water. In the graphs and in the calculations, the amount of dissolved and colloidal substances added with the pressurized water was taken into account.

Fig. 2a and *Fig. 2b* summarizes the flotation efficiency in terms of residual turbidity of the subnatant after flotation. The turbidity decreased with increasing polymer dosage, indicating that the air bubbles after flocculation of the particles lifted the colloidal unstable particles and flocs to the surface.

Using Poly-DADMAC as the flocculation agent DAF reduced the turbidity of pressate water by only 7% at a polymer concentration of 20 mg/l. On the other hand, using C-PAM as flocculation agent the DAF reduced the turbidity by 95% at a polymer concentration 75 mg/l. The use of C-PAM in combination with Poly-DADMAC (1:1 mass ratio) gave the best reduction in turbidity (97%) at the polymer concentration 50 mg/l.

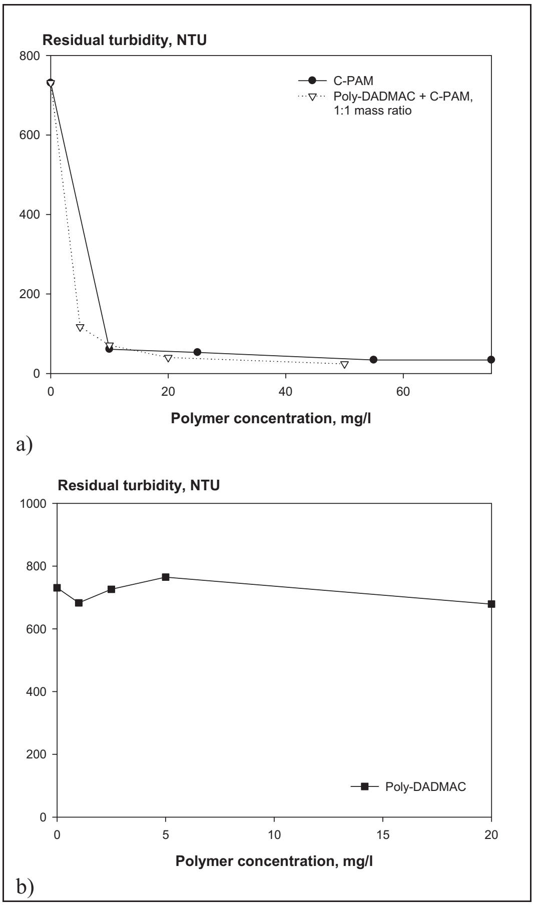

Fig 2. Residual turbidity of Impressafiner pressate water after DAF: a) C-PAM and combination of the polymers; b) Poly-DADMAC.

Fig. 3a and *Fig. 3b* summarizes the flotation efficiency in terms of concentration of extractives in the subnatant after flotation. When Poly-DADMAC was used alone as flocculation agent, the total amount of lipophilic extractives was reduced by about 45% at a polymer concentration of 2.5 mg/l. The concentration was not further reduced by adding up to 20 mg/l Poly-DADMAC.

When C-PAM was used as flocculation agent for Impressafiner pressate water the total amount of lipophilic extractives was reduced by more than 70% at already at a polymer concentration of 10 mg/l. Adding more polymer slightly increased reduction to reach 75% at a polymer concentration of 75 mg/l.

C-PAM in combination with Poly-DADMAC (1:1 mass ratio) behaved roughly in the same way as C-PAM alone and gave the best reduction in total amount of lipophilic extractives for Impressafiner pressate water (76%) at polymer concentration 50 mg/l.

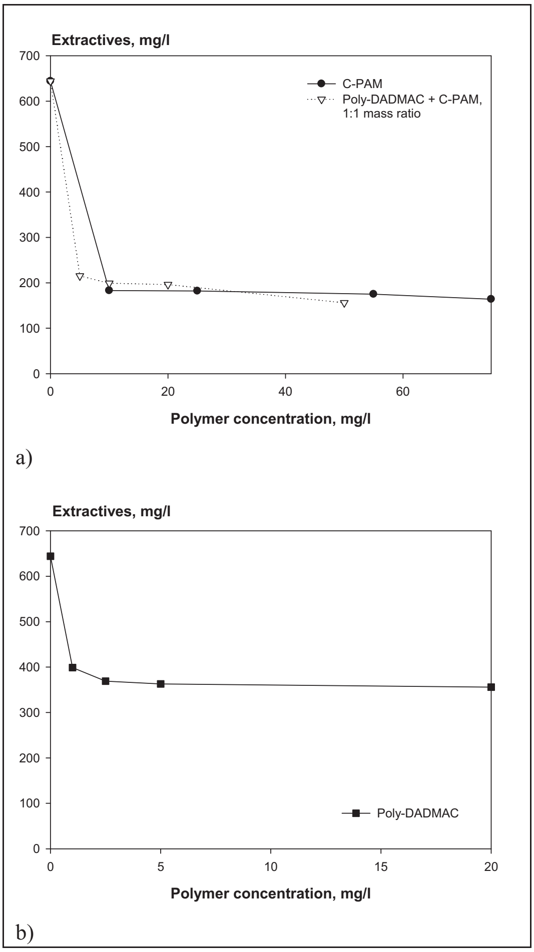

Fig 3. The amount of lipophilic extractives in Impressafiner pressate water after DAF: a) C-PAM and combination of the polymers; b) Poly-DADMAC.

Fig. 4a and *Fig. 4b* summarizes the flotation efficiency in terms of the concentration of carbohydrates in the subnatant after DAF. The lowest reduction of carbohydrates was obtained when using Poly-DADMAC as flocculation agent. The amount of carbohydrates was reduced by 55% already at a polymer concentration of 2.5 mg/l, but then remained the same up to the maximum concentration of Poly-DADMAC added (20 mg/l). When C-PAM was used as flocculation agent the amount of carbohydrates was reduced by 66% when 10 mg/l was added, the concentration then remained constant up to at a polymer concentration of 75 mg/l.

The combination of the polymers (C-PAM + Poly-DADMAC) gave about the same reduction as C-PAM alone. The amount of carbohydrates was reduced by 67%, at a polymer concentration 50 mg/l.

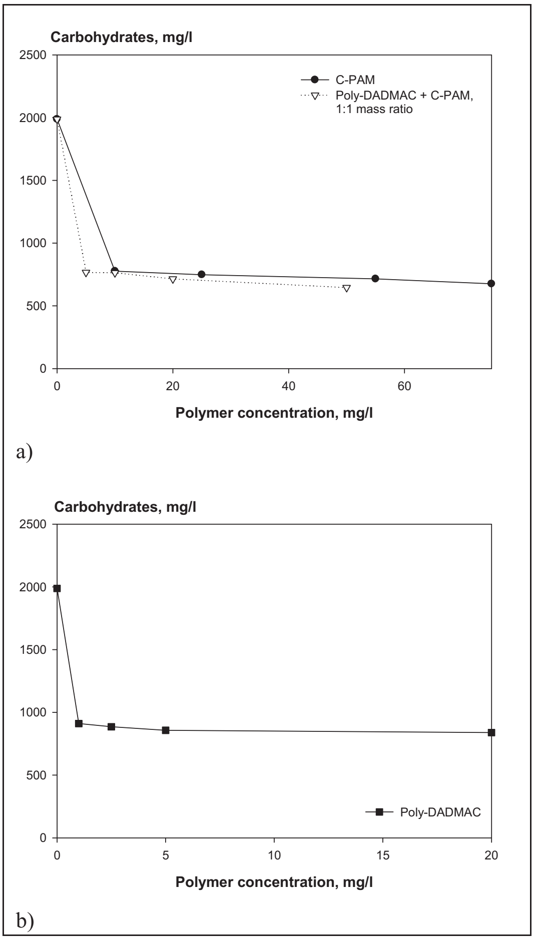

Fig 4. The amount of carbohydrates in Impressafiner pressate water after DAF: a) C-PAM and combination of the polymers; b) Poly-DADMAC.

The amount of lignin after flotation is shown in *Fig. 5a* and *Fig. 5b*. C-PAM and the combination of the polymers reduced the amount of lignin by about 66% at the lowest additions of polymer used. Additional C-PAM did not further reduce the amount, but with the combination of polymers the reduction increased slowly to reach 71% at the polymer concentration 50 mg/l. Poly-DADMAC reduced the amount of lignin by 60% at polymer concentration 2.5 mg/l with no further reduction when the polymer concentration was increased to 20 mg/l.

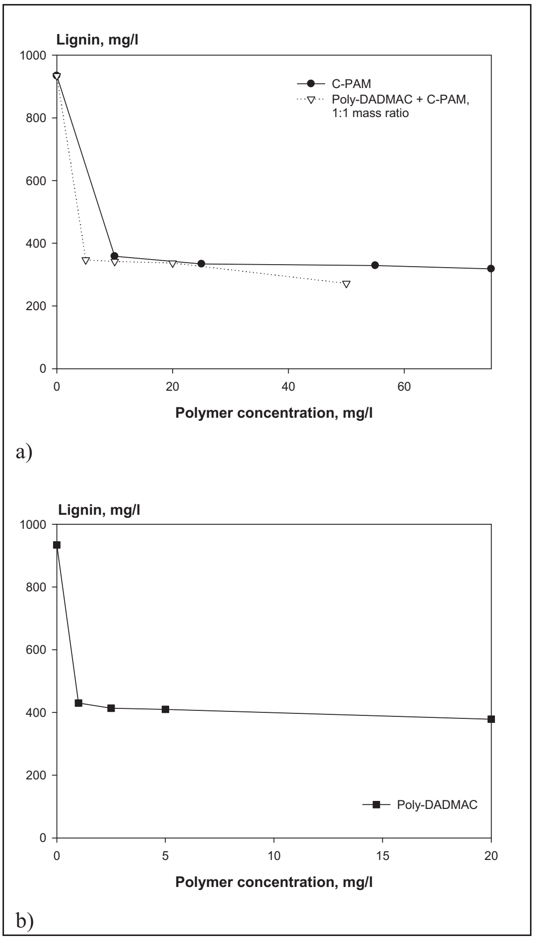

Fig 5. The amount of lignin in Impressafiner pressate water after DAF: a) C-PAM and combination of the polymers; b) Poly-DADMAC.

Fig. 6a and *Fig. 6b* summarizes the flotation efficiency in terms of chemical oxygen demand (COD). Adding C-PAM alone resulted in a reduction of COD by about 71% at the lowest polymer dosage used. Additional C-PAM did not further reduce the COD level. The combination of polymers was slightly less efficient at low polymer concentration, but reduced the COD by the same amount as C-PAM alone at 50 mg/l. When Poly-DADMAC was used alone as flocculation agent, the COD was reduced by approx. 60% at the lowest polymer concentration added. There was no further reduction up to the highest polymer concentration 20 mg/l.

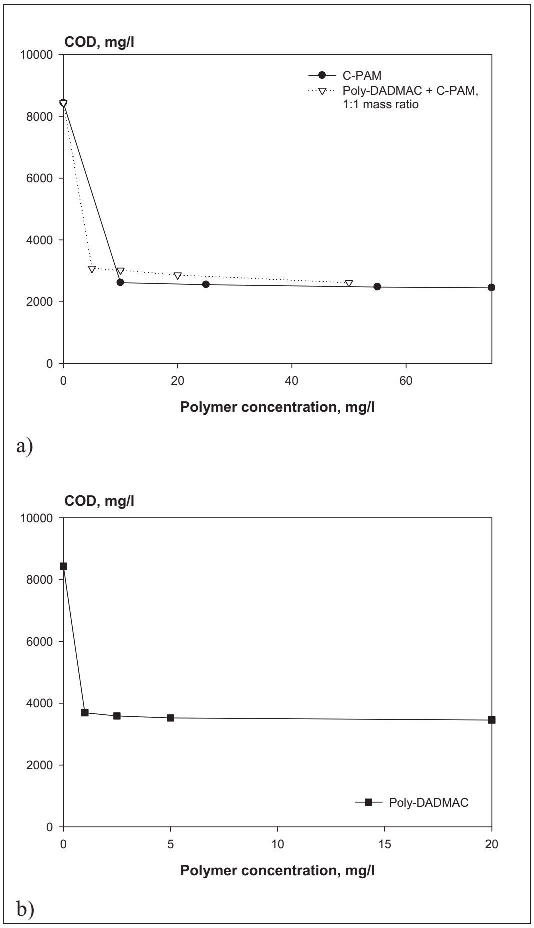

Fig 6. COD of Impressafiner pressate water after DAF: a) C-PAM and combination of the polymers; b) Poly-DADMAC.

The contribution of extractives, carbohydrates, lignin and lignans to the total COD levels were calculated using the conversion factors (Lenes et al. 2001). We have found that approx. 40% of the COD was given by carbohydrates, 30% of COD was given by extractives and 30% by lignin.

Discussion

Comparison of pilot and laboratory trials

The results presented in *figs. 2-6* show that substantial amounts of dissolved and colloidal substances were removed from the Impressafiner water by flocculation with cationic polymers followed by DAF. The reductions of dissolved and colloidal substances after DAF are qualitatively in agreement with those obtained previously in laboratory scale experiments with Impressafiner water taken earlier from the same mill. In both cases it was evident that there was no direct correlation between the amounts of polymer required to achieve efficient flotation and the isoelectric point of the colloidal particles.

Quantitatively there are differences between the experiments that yield some insight into the flocculation mechanism. To facilitate further discussion relative changes in the properties of laboratory and pilot trial waters after addition of 20 mg/l polymer are compared in *Table 4*. This concentration was chosen because it was the highest concentration of pure Poly-DADMAC used in the pilot trial and there was little change in properties when adding higher concentrations of the other polymers.

Table 4. Relative reductions in properties of pressate water from Impressafiner (%), after addition of 20 mg/l of flocculating polymer. Data for laboratory scale experiments from Tanase et al. (2011b).

	C-PAM		C-PAM + Poly-DADMAC, mass ratio 1:1		Poly-DADMAC	
	Lab	Pilot	Lab	Pilot	Lab	Pilot
Turbidity	66	93	82	94	26	7
Extractives	53	65	61	62	34	45
Carbohudrates	31	48	42	50	29	58
Lignin	16	43	22	42	44	59
COD	36	58	51	53	37	59

The first important difference is that turbidity was only marginally decreased by addition of Poly-DADMAC alone in the pilot experiments. This could also be visually observed: after flotation with Poly-DADMAC the water was still turbid without any visible flocs while addition of C-PAM or the combination yielded large, visible flocs and a clear subnatant. In the laboratory trial the turbidity decreased continuously on further addition above 20 mg/l to reach 80% at 100 mg/l Poly-DADMAC. Nevertheless, the chemical analyses showed that extractives, carbohydrates and lignin were removed by the pilot DAF after addition of Poly-DADMAC.

The most likely explanation is that Poly-DADMAC, which is a relatively low molecular mass and high charge density polymer, reacted preferentially with dissolved carbohydrates and to some extent with extractives, forming small, compact flocs, while the polymer did not flocculate the small fibre fragments that, hence, remain in the water after flotation and contribute strongly to turbidity.

The water used in the laboratory experiments had been frozen before the experiments. It is therefore very likely that the amount (and state of aggregation) of fines in the water used in laboratory trial might have been different from the amount of fines in the water taken directly from the mill. Such differences have been reported earlier in the literature (Willför et al. 2006).

Solubility of extractives

Factors such as pH and temperature of the Impressafiner pressate water may also be part of the explanation of differences in the efficiency of the DAF.

Laboratory DAF results showed that 40-45% of the extractives in Impressafiner pressate water were fibre bound, 35-40% were in colloidal form and 13-15% were dissolved.

The Impressafiner pressate water used in the pilot DAF trial contained 45-50% of fibre bound extractives, 30-35% extractives in colloidal form and 17-20% dissolved extractives.

In the pilot DAF trial the pH of the Impressafiner pressate water was 6.6 which was higher that in the laboratory tests (pH 5.5). Moreover, the pH of the air-pressurized water used in the pilot trial was 7.1. It was shown by Sundberg et al. (2009) that the pH of the process water affects not only the degree of dissociation of the carboxyl group but also determines the phase distribution of fatty and resin acids between the water phase and the colloidal phase, see *fig 7*.

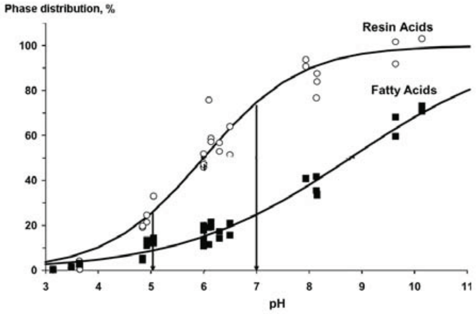

Fig 7. The phase distribution of fatty and resin acids (adapted from Sundberg et al. 2009)

In accordance with the results in *Fig.7,* our pilot DAF results show that the concentration of dissolved extractives in the Impressafiner pressate water was higher than in the laboratory experiments (17-20%) compared with laboratory results (13-15% dissolved extractives). It seems that the phase distribution of extractives affect the efficiency of DAF. In agreement with our results, Richardson and Grubb (2004) have shown that the phase distribution of extractives between fibre bound, colloidal and dissolved affect the efficiency of DAF and that the fibre bound and colloidal extractives can be removed with a removal efficiency of 80-90%. However, the dissolved extractives were removed with a very low efficiency (30%).

The temperature of the Impressafiner pressate water may also affect the efficiency of DAF. Experiments in the pilot trial were carried out at 70°C while laboratory experiments were carried out at 25°C. Negro et al (2005) noted the solubility of air in the pressurized water will be lower at higher temperature. This may also contribute to the lower removal efficiency at the higher temperature. For example, at 6 bar the amount of air in saturated water at 20°C is 36% higher than the amount at 40°C (Ross et al. 2000). On the other hand, the higher temperature of the process water implies that the kinetics of the flocculation (collision rate) is faster.

The reduction in the COD involves the removal of negatively charged particles present in the TMP process water. Thus, the removal of wood extractives significantly contributes to COD reduction.

It is known from the literature that washing mechanical pulp (i.e disc filter, screw presses, etc) is a good way to reduce the COD and extractives content in the pulp, but in this case fibre recovery equipment is required (Käyhkö 2002; Braeuer et al. 2008). Fibre recovery implies that the fibre bound extractives are recirculated back into the process.

Flocculation mechanisms

In our previous study (Tanase et al. 2011b) the measurements of particle size distribution of the pressate water from Impressafiner after DAF confirmed that the large flocs (100-1000µm) were efficiently removed by DAF. The higher removal efficiency of large aggregates could be explained by the collision efficiency. Han (2001) showed that the collision efficiency, which is determined by shear forces (mixing) and on the rate at which particles diffuse toward each other, increases as the particle size increases above 1 µm and that the maximum efficiency is obtained when the particles and bubbles are of similar sizes.

Under turbulent mixing the flocs formed by charge neutralization may actually be not formed at all, because attraction is too short range to overcome repulsive hydrodynamic interactions (Stenius 2000). This statement can be a possible explanation on why the single polymer that did not form extensive loops protruding into the solution (Poly-DADMAC) showed the lowest removal efficiency (*Figs. 2* and *3*).

On the other hand the C-PAM-induced bridging flocculation mechanism yields large flocs and removal efficiency is higher. This interpretation is supported by the different flocculation mechanisms observed in the experiments described in our previous papers (Tanase et al. 2011a, b).

The combination of the polymers (Poly-DADMAC+C-PAM) showed the highest removal efficiency (the polymer with the highest ability to remove dissolved and colloidal substances) in terms of total amount of lipophilic extractives in the subnatant after DAF. The difference between this system and C-PAM alone in terms of turbidity decrease was not significant, but the data in Table 4 show that the reduction of extractives, carbohydrates and lignin was actually larger when the combination of the polymers was used.

Notes on application

A theoretical mass balance can be calculated knowing the consistency of the pulp passing through a screw press, which is generally assumed to be 5-6%. In the press the pulp is dewatered to approx. 28-30% consistency. The filtrate from the screw press, having a consistency of ≈ 0.6%, typically contains approx. 4000-

6000 mg/l COD. Thus, for a TMP mill with a production of 700 t/d, it was found that screw press squeezes out high volume of water: the flow of the filtrate from screw press will be approx. 110 l/s and the amount of filtrate will be about 9400 t/d.

On the other hand, with compressive pre-treatment of the chips, using an Impressafiner, it is possible to remove extractives from the wood chips before refining, thus reducing the amount of extractives that enter the pulping and papermaking process. Thus the removal of dispersed extractives can be done from water containing very few fibres. For a TMP mill using as raw material Norway spruce, with a production of 700 t/d, it was found that the water flow from combined Impressafiner+Plug screw is approx. 16 l/s, i.e. the amount of water will be about 1380 t/d. The water contained approx. 6500 mg/l COD. This water was found to contain a substantial amount of extractives (about 15% from the total amount of extractives in the chips). These were mainly resin acids which thus could be removed from the chips at an early stage into a small volume of water, while fatty acids remained in the chips (Tanase et al. 2010). Resins acids are generally regarded as the main acute toxicity contributors in TMP effluents (Magnus et al. 2000). Extractives removal efficiency may be further improved by adding chemicals between Impressafiner and Plug Screw. Further, Plug Screw can squeeze out higher volume of water by increasing the compression ratio.

When using either a screw press or an Impressafiner, the COD and extractives are transferred from the chips/pulp into the process water. Both filtrates from screw press and pressate water from Impressafiner can be sent to a DAF unit, in order to reduce the amount of extractives and COD from the process water, before the water is sent to the effluent treatment or reused internally in the mill. However, the difference is that a screw press generates high volume of water which implies lower efficiency in DAF and higher amounts of COD and resin acids that are sent to the effluent treatment. Reducing COD with one tonne in an effluent plant requires about 1 MWh of energy. Therefore, an effective DAF can reduce the energy needed in the effluent plant. Moreover, large volumes of the process water imply large investments cost for DAF unit and for the flocculation chemicals.

Having a concentrated water stream, such as Impressafiner pressate water, the COD and the amount of extractives are reduced in the beginning of the process, before refining. As a consequence, treatment of Impressafiner pressate water can be done by using small amounts of polymer and smaller DAF unit. Moreover, by reducing the amount of extractives from chips into the water phase and by using DAF unit for treatment of concentrated water stream, the energy consumption required for running a DAF unit is reduced seven times compared with using a DAF unit for treatment of water from a screw press. Thus the total cost is reduced and DAF efficiency is improved.

Conclusions

The pilot trial confirms that extractives and carbohydrates released into water during compressive pre-treatment of wood chips in fibre bound, dissolved or colloidal form can be efficiently removed by flocculation and DAF. This is verified by decrease of COD values, turbidity, amount of extractives, carbohydrates and lignans. Optimization of the process is necessary for high efficiency of DAF.

The removal efficiency depends highly on the type of flocculating polymer used. Moreover, the optimization of coagulation and flocculation is necessary for optimum performance of flotation system.

The best removal efficiency is obtained with a combination of the polymers (Poly-DADMAC + C-PAM, mass ratio 1:1). Using a low molecular mass and high charge polymer (Poly-DADMAC) alone also removes dissolved and colloidal substances, but is less efficient in reducing turbidity.

Factors such as pH and temperature of the pressate water will affect the phase distribution of wood extractives (colloidal, dissolved or attached to fines and fibres) and the efficiency of DAF.

In summary, using DAF for separate treatment of water from the Impressafiner could play an important role in the treatment of process water streams, since it efficiently removes extractives from a process water with relatively high concentration of extractives, and thus reduces the risk of a build up of these in the TMP process water loops.

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Paper V

Opedal Tanase M., Stenius P., Johansson L. (2011): Review:
Colloidal stability and removal of extractives from process water in thermomechanical pulping, Nordic Pulp and Paper Research Jornal, submitted

REVIEW: Colloidal stability and removal of extractives from process water in thermomechanical pulping

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KEYWORDS: Thermomechanical pulping, extractives, dissolved air flotation, steric stabilization, electrostatic stabilization, turbidity

SUMMARY: This paper reviews the literature on the effect of the removal of colloidal wood extractives from thermomechanical process water by using a dissolved air flotation unit. The primary aim is to understand the mechanism behind the stability of the colloidal wood extractives present in the process water. Different analytical methods to study the colloidal stability of extractives are described. The problems caused by wood extractives (pitch) during the TMP process are discussed in relation to stability of colloidal wood extractives. Mechanical pulping pre-treatment and impregnation technology are discussed in relation to reduce the amount of extractives from the wood chips as early as possible in the beginning of the TMP process, in order to reduce the detrimental effects of extractives.

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During mechanical pulping processes up to 5% of the wood material are released into the process waters. Thus, in typical modern thermomechanical pulp (TMP) mills with capacities of 500-700 t/d, tonnes of materials daily end up in the process water. This material consists of carbohydrates, low-molar mass organic acids, pectic acids, lignans, lipophilic extractives and lignin related substances (Thornton 1993). Norway spruce (*Picea abies*), the main species used for mechanical pulp in Europe, contains 1-2% lipophilic extractives that are composed mainly of fatty acids, resin acids, sterols, steryl esters and triglycerides (Sjöström 1993).

Increasing closure of process water circuits in paper mill leads to accumulation of these substances. This may lead to "pitch problems", i.e. formation of deposits, foaming and runnability problems of the paper machine, particularly in the wet end (Holmberg 1999). The enrichment of some of the substances also increases the anionic charge of the papermaking stock and greatly impacts the quality of the final product (Pelton et al. 1980; Sundberg et al. 2000).

Some constituents of the process water (e.g. resin acids) cause increased aquatic toxicity of paper industry effluents (Magnus et al. 2000). Moreover, fatty and resin acids and the corresponding anions are surface-active compounds and in paper they affect the surface properties, such as the binding between fibres, water adsorption, and friction.

Therefore, removal of detrimental substances (i.e. extractives) from process water is of great importance both for the control of effluents and for the improvement of paper machine efficiency. In some cases the total energy consumption during subsequent refining can also be reduced (Sabourin 2000; Sabourin et al. 2002).

Two commonly used ways to prevent detrimental substances from circulating in the white water system and reduce deposition problems ("pitch control") are attachment to the paper web with retention chemicals such as organic polymers, polymers in combination with mineral particles or adsorption onto special pigments (Wågberg and Ödberg 1991; Sundberg et al. 1993). The drawback of using retention aids is that they may have a negative effect on paper qualities such as absorbent papers (Holmbom and Sundberg 2003).

Washing mechanical pulp is another way to remove extractives (Käyhkö 2002), but the increased closure of water circuits implies that washing mechanical pulp requires fibre recovery. One result of fibre recovery is that fibre bound extractives in the process water can be recirculated back into the process, thus rendering removal of extractives less efficient.

A conclusion that can be drawn from the problems associated with these methods of pitch control is that in order to achieve high closure it will be advantageous to eliminate harmful substances or at least to decrease their negative effect as early as possible in the process.

Using equipment for compressive pre-treatment of the chips (i.e. plug screw) offers the possibility to remove some of the extractives from the wood chips before refining, thus reducing the amount that enters the pulping and papermaking processes. A few reports have been published regarding removal of extractives during compression of chips in a screw feeder (Cisneros and Drummond, 1995; Thornton and Nunn 1978). In 1997 Andritz introduced a revised type of compression screw equipment, the so-called called RT Impressafiner.

Using this equipment, it is possible to remove extractives from the wood chips before refining without loss of fibres (Sabourin et al. 2002; Tanase et al. 2010). A mass balance of extractives in a spruce TMP mill with a capacity of 700 t/d (Tanase et al. 2010) revealed that 7 t of extractives entered the mill every day and

15% of the lipophilic wood extractives (~ 1 t/d) were enriched in the process water after compressive pre-treatment. Obviously, treatment of this water it is important in order to avoid that the extractives enter the effluent treatment or reach undesirable levels in the process water.

Flotation, clarification, membrane filtration or evaporation can be used as internal cleaning stages. The purified water can then be reused in the TMP process.

This review summarizes the factors governing the stability of wood extractives present in process water, its effect on deposition tendency and paper strength and different ways to remove the extractives from the process water with emphasis on dissolved air flotation (DAF).

Mechanical pulping and impregnation

Mechanical pulping is an energy-intensive process. Energy requirements for a given product quality are determined by the quality of raw material, the action and efficiency of pulping equipment and the pulping process (Milles and Karnis, 1995).

Mechanical pulping is accomplished in two distinct processes: separating or breaking down the wood into its basic constituents (mainly fibers) and transforming the individual fibers into suitable pulps for papermaking. These processes are defined as defibration and fibrillation, respectively. Most of the energy is consumed in the latter fibrillation stage. Both defibration and fibrillation of fibers take place during primary refining of wood chips. As discussed by, among others, Stationwala et al. (1993) and Heikkurinen et al. (1993) defibration of wood chips during the initial stage i.e., primary refining, is crucial for determining final pulp quality and energy consumption. Indeed, the primary refining step can be said to establish the “footprint” of thermomechanical pulp quality (Karnis, 1994).

Effects of compressive pre-treatment on wood and fibre morphology were first described by Frazier and Williams (1982). Sabourin (1998) and Kure et al. (1999) showed that pressurized compressive pre-treatment combined with high intensity refining is an efficient way to reduce energy consumption in thermomechanical pulping. The RT Impressafiner is designed to preheat the chips (retention time 15 s, pressure 1.5 bar) and compress the chips to a uniform size distribution as they proceed to the discharge of the screw press (Sabourin 1998). The purpose is to open up the wood chip structure before refining, to minimize variation in moisture content, maximize the removal of extractives, reduce variation in bulk density and reduce the energy consumption during subsequent refining (Sabourin 1998, 2000).

Compressive pre-treatment also facilitates impregnation of the chips with chemicals. There are two distinct mechanisms involved in chip impregnation. The first one is rapid and essentially involves the penetration of liquor through voids and capillaries, while the other is much slower and involves diffusion of the chemicals through the cell walls (Barbe et al. 1993; Peng and Granfeldt 1996).

A uniform impregnation of the wood chips is important in order to achieve higher fiber flexibility and pulp strength as well as lower consumption of bleaching chemicals (Barbe et al. 1993; Parkinson et al. 1996; Zanuttini 2005). This is commonly achieved using a screw press impregnator, in which the wood chips are compressed and then expanded in the impregnation liquor. Experience of high-yield pulping has shown that this treatment improves the chemical uptake and the uniformity of chemical distribution in the wood chips. The strength properties of the resulting pulp are also positively affected and in some cases the refining energy consumption can be reduced. The degree of deformation depends partly on the compression ratio, and partly on the treatment of the chips prior to the screw press. The liquor/air extraction, caused by compressive stresses, is considered to facilitate the uptake of impregnation liquor and chemicals (Barbe et al. 1993). Furthermore, the chemical uptake into the different fractions is significantly improved by using a higher compression ratio (i.e. 5:1 instead of the 3:1). Thus it is advantageous to have a good chip breakage in order to improve chemical impregnation, as a more uniform chemical concentration within the chips leads to higher pulp quality. Chip breakage also results in the release of dissolved and colloidal matter from the chips.

Dissolved and colloidal substances in mechanical pulps

The dissolved and colloidal organic substances in circulating waters in TMP mills have been well characterized in several studies (Sjöström 1990; Nylund et al. 1993; Thornton 1993; Sundberg et al 1993; Sihvonen et al.1998; Back 2000).

The major substance group in deposits has been indentified as wood extractives, composed mainly of free fatty (~ 6%) and resin acids (~10%), sterols, steryl esters and triglycerides (Qin et al. 2003).

At low pH most of these compounds are completely insoluble in water. The acids dissociate and dissolve partially at pH > 7-8 (Sundberg et al. 2009). Thus, at papermaking pH values, and under the conditions prevailing in e.g. an Impressafiner the lipophilic extractives will be manly released as dispersed, hydrophobic, microscopic (colloidal) particles (“pitch particles”) or bound to fibre fragments in the process water (*Fig. 1*) (Laubach and Greer 1991).

Colloidal pitch particles carry a negative surface charge and in a thermodynamically unstable, kinetically stabilised state. Several different factors can cause elimination of the stabilising mechanisms. As a result the colloid “breaks”, i.e. the particles form large aggregates that may end up as sticky deposits in a paper machine system (*Fig. 2*) or occur as impurities in the final product (Laubach and Greer 1991).

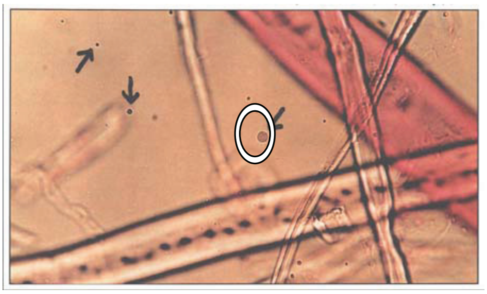

Fig 1. Colloidal pitch particles dispersed in white water (adapted from Laubach and Greer 1991).

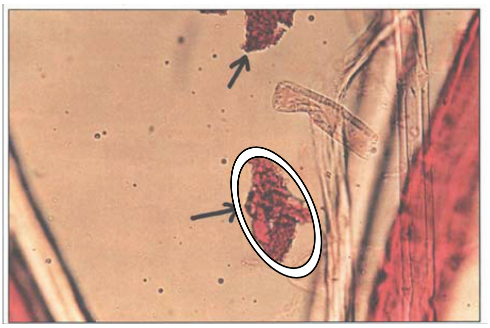

Fig 2. Pitch agglomerates in a machine chest stock sample (adapted from Laubach and Greer 1991).

The amount of insoluble ("lipophilic") extractives released during pulping depends on the type of wood being pulped. Softwoods generally contain a larger amount of extractives (due to the presence of resin canals in the wood), but hardwood pitch is often more difficult to treat due to its generally higher levels of insoluble neutral organic pitch components (e.g., waxes, fatty alcohols, sterols and resin acids) that form a very sticky mixture (Laubach and Greer 1991).

Colloidal stability of wood extractives

1. Factors affecting colloidal stability

Wood extractives may be dissolved in the process water, attached to fines and fibres or exist as suspended colloids in the size range of 0.1-1 µm (Nylund et al.1993; Swerin et al. 1993). A proper understanding of the colloidal stability, i.e. the factors controlling the tendency of these colloidal particles to agglomerate or remain suspended, is of great importance for the control of whether or not the extractives present may deposit to form troublesome pitch deposits and of how they can be separated from the process water.

Whether a colloidal dispersion remains stable or not depends on a balance of attractive and repulsive interactions between the particles.

If the attractive interactions are stronger than the repulsive ones particle collisions will lead to particle growth. The rate of growth depends on particle concentration (i.e. frequency of particle collisions due to diffusion), hydrodynamic conditions and the range of action of the attractive interactions. Properties of process water that affect these interactions are particle concentration and surface properties, pH, electrolyte concentration, temperature, viscosity and chemical composition of the extractives and the presence of adsorbing wood polymers or polymeric additives (Allen 1979; Blanco et al. 2005). Eventually, attachment of particles to each other leads to formation of large aggregates that may separate and, e.g., form deposits. Attraction may of course also lead to direct attachment of colloidal particles to solid surfaces (machine equipment, fibers).

The best understood surface interactions that influence colloidal stability are those due to Van der Waals forces, diffuse ion layers at charged surfaces, and adsorbed or dissolved polymers. Other important but theoretically less well clarified interactions are effects of solvation and hydrophobic interactions (Stenius 2000).

2. Van der Waals interactions

The Van der Waals forces between extractive particles in aqueous solution are always attractive and, in comparison to the typical thickness of surface layers, long-range (tens of nanometers). Whether the colloid is stable or not will therefore depend primarily on whether the other interactions give rise to sufficiently strong repulsion.

3. Electrostatic stabilization

Under papermaking conditions dissolved wood polymers as well as dissolved or dispersed extractives are negatively charged, predominantly due to the dissociation of carboxylic groups in fatty acids, resin acids and hemicelluloses (Sundberg et al. 2000). Dissociation of fatty and resin acids in the surfaces of extractive particles leads to the formation of a negative surface charge and a diffuse layer of small mobile ions in the surrounding electrolyte solutions close to particle surface. This layer is enriched in cations and depleted in anions. When two particles collide the diffuse layers repel each other, thus preventing particles from attaching to each other. Diffuse layers are compressed when the electrolyte concentration increases and for the repulsion to be sufficiently strong, the concentration should be below ≈ 0.1 M of 1:1-electrolyte and below ≈ 0.01 M of 2:1 electrolyte, where the divalent ion is a cation (Hiemenz and Rajagopalan 1997; Stenius 2000).

An increased amount of fatty and resin acids will increase the surface charge density of the colloidal wood resin resulting in increased stability of the colloidal droplets (Sihvonen et al. 1998). However, increased protonation of the carboxylate ion of fatty and resin acids at pH below 5 decreases the surface charge of the colloids. Then the colloidal wood resin is no longer electrostatically stabilized and aggregates

(Johnsen et al. 2004). *Fig 3* shows the influence of pH on the stability of colloidal wood resin.

Thus, electrostatically stabilized colloidal wood extractives, can be destabilized at relatively low electrolyte concentrations. Another way of reducing electrostatic interactions is based on the use of cationic polymers that neutralize the surface charge by adsorption or to introduce attractive forces, such as bridging. On the other hand, adsorption of excess polyelectrolyte may lead to restabilization (Stenius 2000).

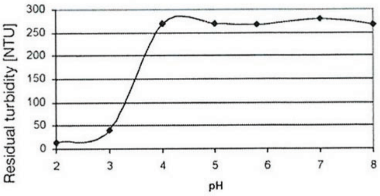

Fig 3. Effect of pH on the stability of the colloidal wood resin (Johnsen et al. 2004). Residual turbidity is proportional to the concentration of colloidal particles in the water after centrifugation

4. Steric stabilization

Another important stabilization mechanism of colloidal dispersions is steric, or polymer stabilization (Shaw 1980; Hiemenz and Rajagopalan 1997). This is due to the adsorption of soluble polymers on the particle surface. Such layers repel each other when particles collide. This type of repulsion is effective even at very high salt concentrations.

Pure dispersions prepared from the colloidal wood extractives) are electrostatically stabilized (Sundberg 1995). However, particles from TMP often do not agglomerate even at high salt concentrations. This stability against salt is due to steric stabilization.

The adsorption of hemicelluloses on extractive colloids and their stabilizing effect on colloidal wood resin has been studied extensively (Johnsen et al. 2004; Sihvonen et al. 1998; Sundberg et al.1994a; Sundberg et al 1994b). The steric stabilization of colloidal resin is due to adsorption of dissolved hemicelluloses, especially galactoglucomannans (Pelton et al. 1980; Hannuksela et al. 2004; Sundberg et al. 1996; Allen 1979; Swerin et al. 1993; Holmbom and Sundberg 2003) and prevents the colloids from aggregating at the addition of salt even when the electrostatic forces become insignificant. The stability of resin reduces its ability to form deposits (Otero et al. 2000).

This is illustrated by *fig. 4* and *fig. 5* which show the residual turbidity after centrifugation of a solution containing DCS. Turbidity decreases only slightly even at high electrolyte concentrations for unbleached suspensions, whereas complete aggregation of colloidal substances from peroxide bleached TMP is observed upon addition of sufficient amount of $CaCl_2$ and $LaCl_3$ (Sundberg et al. 1994b, *Fig. 4* and *Fi.g 5*).

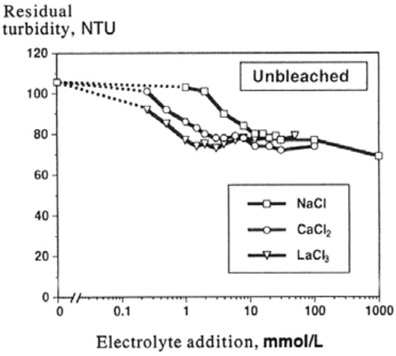

Fig 4. Turbidity of colloidal substances from unbleached TMP (Sundberg et al 1994b).

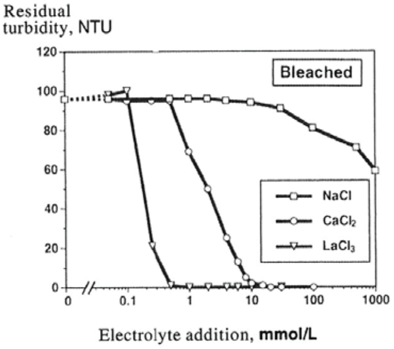

Fig 5. Turbidity of colloidal substances from peroxide bleached TMP (Sundberg et al 1994b).

5. Hydrophobic interactions

The material in lipophilic extractives is insoluble in water and strongly hydrophobic, i.e. it is not wetted by water. The reason for the hydrophobicity is that the cohesive forces in water are much stronger than those between hydrocarbon chains. As a result particles may be held together or attach to hydrophobic surfaces because they are “forced out” from water by the strong cohesion between the water molecules. This type of interaction is denoted “hydrophobic interaction” and probably contributes strongly to the tendency of pitch particles to form deposits. It also leads to the enrichment of hydrophobic particles at water surfaces (Kallio et al. 2004).

6. Flocculation with polymers

Polymers are often also used to induce aggregation (flocculation) of colloidal particles either, as mentioned above, by charge neutralisation or by forming bridges between the particles. Flocculation by bridging is a very efficient mechanism, in particular when the goal is to unselectively flocculate as much of the colloidal material in a suspension as possible. Bridging flocculation is therefore extensively used in water treatment, in order to create large flocs that can be easily removed by sedimentation, filtration or flotation (Tripathy and De 2006). Bridging flocculation is also the main mechanism by which most retention chemicals used in papermaking function (Hubbe 2007). Both polyelectrolytes and non-ionic, water-soluble polymers can be used as bridging flocculants. The essential requirement is that the polymer attracts simultaneously to two particles, which in general requires the polymer to have a high molecular weight and to maintain an extended conformation in solution. For flocculation of anionic particles the most commonly used polymers are cationic polyelectrolytes with low charge density, such as cationically modified polyacrylamides, copolymers of glucosamine and acetylglucosamine (chitosan), poly-ethylene imine etc.

In a sheared suspension, flocculation may occur quite rapidly, but the flocs eventually reach a limiting size and no further flocculation occurs. This limiting size depends on the applied shear rate and on the strength of the flocs (Gregory 1988). In some cases, because of the irreversible nature of floc breakage, flocs are unable to re-grow if broken at a higher shear rate (Jarvis et al. 2005).

Floc strength is an important property in separation processes since break-up of flocs can affect the efficiency of the separation process. Thus, for example, flocs formed for removal by flotation that subsequently break-up into many smaller flocs may be captured less efficiently by air bubbles.

Methods to study colloidal stability of extractives

The colloidal stability of dispersions is usually investigated by measuring the rate of growth and sedimentation or creaming of the particles under different conditions. One way to describe the stability of colloids can be e.g., to observe their aggregation behaviour in the presence of simple electrolytes, polyelectrolytes or nonionic polymers (Shaw 1980). These methods have also been used to study the stability of extractives in process water.

Turbidity measurements. TMP process water generally is turbid i.e. light is strongly scattered by the water. The scattering intensity mainly depends on fibre fragments (fines) and particles formed by insoluble extractives released from the chips. Thus, it has been shown that the concentration of lipophilic extractives correlates well with the turbidity of water samples when no fillers or fines are present in the sample (Örså and Holmbom 1994; Sundberg et al. 1994 and 1996; Sundberg 1995; Sundberg et al. 1993; Mosbye 2003; Johnsen 2007).

Turbidity measurements can in many instances replace the more tedious determination of extractive concentrations by e.g. chromatography. Moreover, turbidity measurements carried out after centrifugation can also be used to follow the effect of coagulants or stabilizers on pitch particles. Scattering of electromagnetic radiation by particles generally is strongest if the particle size is similar to the wavelength of the light (Bohren and Huffman 1983) and increases with increasing particle size. Thus, visible light (wavelength 390-750 nm) is strongly scattered by colloidal particles in this size range, which is typical for colloidal pitch (Allen 1979). Thus the turbidity will increase with aggregation of particles, before it falls off to low values under conditions of complete aggregation and separation of the particles (Sihvonen et al. 1998).

Turbidities are monitored with common UV-Vis spectrometers or in specially designed instruments for detection of light scattering. A more detailed monitoring of sedimentation rates can be obtained with the *Turbiscan* instrument, which records forward and back scattering of light along the whole length of a vertical sample tube. This method detects and characterizes also relatively rapid destabilization phenomena affecting the homogeneity of dispersions such as particle migration (creaming, sedimentation) and particle size variation or aggregation (coalescence, flocculation) (Mengual et al. 1999; Xu et al. 2007; Tanase et al. 2011a).

Light microscopy at suitable magnifications can yield quick information on pitch particle size, degree of agglomeration and presence of particulate additives (Sithole 2000). However, flocculated colloidal particles (aggregates) are difficult to measure accurately, since they are easily restructured, often due to break-up.

Flow cytometry (FCM) is an analytical method that allows the rapid measurement of light scattering and fluorescence emission produced by suitably illuminated cells. The cells, or particles, are suspended in liquid and produce signals when they pass individually through a beam of light. The scattered light and fluorescence emissions are collected by detectors and are sent to a computer, where the distribution of the population with respect to the different parameters is represented. FCM might be a rapid method for analyzing paper mills process waters, providing an early warning of microbiological as well as chemical deposit formation (Lindberg et al. 2004).

The *Coulter* principle is the most common stream scanning technique, in which the change in electrical resistance as particles flow through a small orifice is measured and related to particle volume (Ljunggren 2006).

Removal of extractives from process water

Apart from binding them in to the paper web, dissolved and colloidal substances can be removed from the process water by sedimentation, filtration, flotation, and reverse osmosis. From a technological point of view the choice of the cleaning technique depends on which process stage that is best suited for deresination of the wood fibre and concentration of extractives in the specific process water at each mill.

Clarification (settling, sedimentation) is a process based on the density difference between solid particles and water. Solid matter settles to the bottom, from where it is removed. In pulp and paper industry the most common type of external treatment is mechanical clarification. The process can be divided into there stages: pretreatment, clarification and sludge handling. Finely suspended material that does not settle satisfactorily requires either mechanical flocculation or the addition of chemicals. The sludge obtained from clarification is usually thickened, dewatered and then either used or disposed of (Pertti 1998; Ljunggren 2006).

Straining and filtration can be used in fibre recovery and in the external treatment of effluents with high solids contents. In the production of fresh water for the pulp and paper industry, the flocs that have passed through with the clarified water from chemical treatment are removed by filtration. However, finely suspended solids and pitch often cause problems by blocking the filter (Pertti 1998; Ljunggren 2006).

Ultrafiltration is a process that allows emulsified, suspended, colloidal and high molecular mass material to be removed from a solution by means of a porous membrane. Solvent molecules and low molecular mass compounds pass through the membrane, causing the larger material to become more concentrated. Ultrafiltration produces two fractions: concentrate and permeate. The concentrate contains all material unable to pass through the membrane, while the permeate contains those molecules that have passed through (Pertti 1998).

Dissolved Air Flotation, DAF, is a process that removes detrimental components by attaching them to micro bubbles generated when a pressurized solution of air in water is released into the flotation cell. DAF commonly used in process where it is desired to rapidly remove as much as possible of the colloidal particles from a suspension.

Flotation of particles smaller than a few µm is inefficient because hydrodynamic effects on particle collisions decrease the probability of attachment of small particles to much larger bubbles (Han 2001; Rao 2004), and thus particles smaller than that, such as colloidal extractives, have to be flocculated before flotation.

In papermaking, DAF is often used in deinking processes and external wastewater treatment plants. In water treatment DAF is used for primary clarification and in wastewater treatment DAF is applied for sludge thickening, secondary clarification and as polishing after secondary clarification (Lundh et al. 2000).

DAF has also been beneficially applied for removal of extractives from thermomechanical process waters: cloudy white water (derived primarily from the disk filter that concentrates pulp after the cleaners) and reject filtrate (derived from concentrating the fibre prior to reject refining) (Richardson and Grubb 2004), in a eucalyptus kraft mill in order to control pitch deposition (Negro et al. 2005) and for removal of detrimental substances from peroxide-bleached thermomechanical pulp water (Saarimaa et al. 2006). It was found that 80-90% of the fibre-bound and colloidal extractives could be removed in this way.

Flocculation in DAF can take place by different mechanisms, including charge neutralization, bridging, and complex flocculation. A wide range of chemicals have been developed in order to flocculate dissolved and colloidal substances and to remove them from the system by using DAF. Common chemicals include aluminium sulfate, ferric chloride, aluminium based products such as poly-aluminium chloride (PAC), minerals such as bentonites or talcs and organic polymers such as cationic polyacrylamide (C-PAM), poly-(N-N-dimethyldiallyl-3-4-ethylenpyrrolidonium)-chloride (poly-DADMAC), polyethylene oxide (PEO), etc. The use of cationic polymers as flocculants requires a good knowledge of the polymer properties (charge density and molar mass), the amount added, the dosage strategy and the mixing process (Stenius 2000).

Traditional methods for determining the efficiency of chemical treatments in DAF are based on turbidity measurements, determination of lipophilic extractives and carbohydrates, chemical oxygen demand (COD) and total organic carbon (TOC) are also often measured (Saarimaa et al. 2006).

A number of factors, such as geometrical design, pre-treatment method, air-solid ratio, the collision between bubbles and flocs, pH and temperature of the process water may influence the DAf efficiency. In the following, the collision between bubbles and flocs, pH and the temperature of the process water will be discussed.

The mechanism of dissolved air flotation

The mechanism of dissolved air flotation is to allow micro-bubbles of air attach to the suspended particles in the water. The principle is to develop agglomerates with lower density then water, causing the flocs to rise through the water and accumulate at the surface where can be removed as sludge. The micro-bubbles are generated when a pressurised solution of air in water is released into the flotation cell. A schematic illustration of a DAF unit is represented in *Fig. 6*.

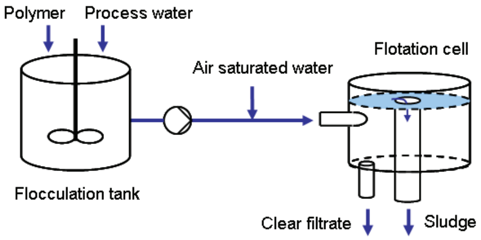

Fig. 6. Schematic illustration of a DAF unit.

The size of the colloidal extractives is generally less than a few µm. Thus, they must be flocculated before flotation. Hence, a flotation tank is used to mix chemicals into the water in order to flocculate and coagulate the substances in the water into larger flocs.

Theory of attachment

Bubbles and particles/flocs attach to each other when colliding. The mechanisms that rule the interaction between bubble and particles is described by Lundh (2002) (*Fig. 7*). The first mechanism (*Fig. 7a*) is the adhesion of bubbles to pre-formed flocs due to attachment forces. This mechanism is believed to work when the particles and bubbles have almost the same size (~ 60 µm). Attachment of bubbles with pre-formed flocs is also believed to work when the particles are larger than ~ 200 µm. The bubbles are caught by the particles because the flocs have a loose structure. The incorporation of bubbles into growing flocs occurs if there is a floc break-up and re-flocculation in the contact zone (*Fig.7b*). The bubbles are caught in the flocs when they re-flocculate. Another type of incorporation occurs if the bubbles are introduced before or during the pre-treatment flocculation.

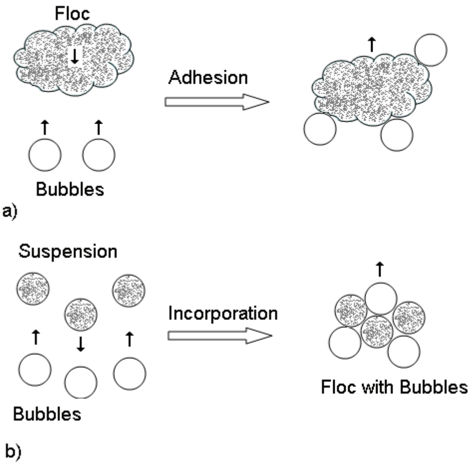

Fig. 7. Schematic model of interaction between air bubble and floc.

Several theoretical considerations and aspects of separation mechanism with reference to the preferable particle size are presented by Fukushi et al. (1995), Haarhof and Edzwald (2001), Han et al. (2001), revealing some disagreement on the preferable floc size for successful removal in DAF units. The general conclusion is that the maximum flotation efficiency is obtained when the particles and bubbles are of similar sizes.

Effect of pH and temperature on the DAF efficiency

The pH of the process water affects the liberation of wood resin, as the resin and fatty acids increases dissociate with increasing pH. The anions (soaps) formed are highly soluble in the presence of monovalent cations only, but the solubility of their calcium salts is low (Lindström et al. 1988; Sundberg et al. 2009).

Thus, Richardson and Grubb (2004) have shown that the phase distribution of extractives between fibre bound, colloidal and dissolved affect the efficiency of DAF and that the fibre bound and colloidal extractives can be removed with a removal efficiency of 80-90%. However, the dissolved extractives were removed with a very low efficiency (30%).

The temperature of the process water may also affect the efficiency of DAF. Negro et al (2005) noted the solubility of air in the pressurized water will be lower at higher temperature. This may also contribute to the lower removal efficiency at the higher temperature. On the other hand, the higher temperature of the process water implies that the kinetics of the flocculation (collision rate) is faster.

Other methods to clean up the process water

Membrane filtration systems have become widely recommended for white water purification. Ultrafiltration membranes are rated to exclude very large molecules, such as polyelectrolytes, whereas microfiltration systems have pore sizes selected to exclude bacterial cells and fine particulate matter suspended in the water. A disadvantage of using microfiltration and ultrafiltration is the fouling phenomena that occur and low volumetric throughput (Pizzichini et al. 2005; Hubbe 2007). Foulants such as bacteria and pitch can occlude the pores of a micro-filter system, due to a similarity in size.

A biological treatment system is well suited to remove low-mass organic molecules, but does not remove low-mass inorganic electrolytes. The output from a biological treatment system is often turbid, and it may contain viable bacteria cells. When used alone, there is a danger of poor dewatering, brightness loss, salt build-up. Thus a second type of treatment is required. However, as part of a system for within-mill treatment of white water, biological treatment can reduce the level of biological oxygen demand (BOD) (Hubbe 2007).

Evaporation systems can produce water that is free of salts and most organic matter (Bourogne 2001), but do not remove low molecular weight alcohols and organic acids. The draw back of the method is the highly cost.

Oxidation is another way to break down various biodegradable materials in white water. When used alone, the oxidation treatment does not remove anything, in some cases makes removal more difficult (Hubbe 2007).

DAF for water clarification is especially effective in the case of particulate matter having some hydrophobic character. It has been found that very small bubbles can be effective for removal of very finely divided matter from aqueous solution. However coagulation and flocculation are necessary for optimum performance of DAF unit. One advantage of using DAF is that the lipophilic extractives are efficiently removed from the process water and thus reduces the risk of a build up of these in the TMP process water loops. An important factor is the location of a DAF unit in the process.

It is known from the literature that washing mechanical pulp (i.e disc filter, screw presses, etc) is a good way to reduce the COD and extractives content in the pulp, but in this case fibre recovery equipment is needed (Käyhkö 2002; Braeuer et al. 2008). Fibre recovery implies that a part of the fibre bound extractives are recirculated back into the process.

On the other hand, with compressive pre-treatment of the chips, using an Impressafiner, it is possible to remove extractives from the wood chips before refining, thus reducing the amount of extractives that enter the pulping and papermaking process, from a process water containing very few fibres. This water was found to contain a substantial amount of extractives (about 15% from the total amount of extractives in the chips). These were mainly resin acids which thus could be removed from the chips at an early stage into a small volume of water, while fatty acids remained in the chips (Tanase et al. 2010).

Another advantage of using DAF gives a clean subnatant which can be recirculated into the process and that the sludge formed is very concentrated in extractives. Thus there is the possibility to recover extractives from the sludge and to use them in synthesis on new molecules, bioactive chemicals, solid fuel, pharmaceuticals.

Conclusions

Mechanical pre-treatment of chips improve chemical impregnation (Sabourin 2000), reduce the extractives content in the chips (Sabourin et al. 2002; Tanase et al. 2010), reduce variation in bulk density and reduce the energy consumption during subsequent refining (Sabourin 1998; Kure et al 1999).

The surface chemistry of the system is naturally an important factor determining the deposition tendency of wood extractives. Interaction with different dissolved substances, of which at least a part are surface active at the air-water interface, contribute to the surface chemistry of the droplets (Nylund 1997).

Dissolved Air Flotation, DAF seems to be a convenient method to remove extractives from thermomechanical process water (Richardson and Grubb 2004; Negro et al. 2005; Sarimaa et al. 2006).

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