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Lappeenranta University of Technology

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THE INFLUENCE OF PROCESS CONDITIONS ON THE DERESINATION EFFICIENCY IN MECHANICAL PULP WASHING

Thesis for the degree of Doctor of Science (Technology) to be presented with permission for public examination and criticism in the Auditorium of the Student Union House at Lappeenranta University of Technology, Lappeenranta, Finland on the 7th of June, 2002, at noon.

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PREFACE

This study was conducted at Lappeenranta University of Technology in the laboratory of Paper Technology between1996 and 2002 in connection with the International PhD Program in Pulp and Paper Science and Technology (PaPSaT).

I wish to express my sincere thanks to professor Hannu Manner for his encouragement, support and guidance during this study. I am also grateful for the valuable comments and corrections provided by the pre-examiners of this thesis, Dr. Kenneth Sunberg and Dr. Raimo Malinen.

A major part of this study was conducted in the CACTUS technology programme which was organised by the *National Technology Agency of Finland* (*TEKES*). I would like to express my gratitude to TEKES and the companies from industry that participated in CACTUS (*Ahlström Machinery Oy, Hadwaco Oy, Kemira Chemicals Oy, M-Real Oyj, Myllykoski Paper Oy, Raisio Chemicals Oy, Stora-Enso Oyj, UPM-Kymmene Oyj, Metso Oy*) for their financial support and also for the pleasant and fruitful co-operation.

The Academy of Finland (International PhD Program in Pulp and Paper Science and Technology) is greatly acknowledged for the financial support it provided. Also, the scholarships awarded by the *Foundation for the Research of Natural Resources in Finland* and *Lappeenranta University of Technology* played a crucial role in conducting and completing this study, and the donors are gratefully acknowledged.

I wish to thank all my friends and present as well as former colleagues in the Department of Chemical Technology for a nice and friendly working atmosphere as well as for the help they provided me throughout these years. I would like to thank Toni Väkiparta, Petteri Kotonen and Pekka Buure who assisted me greatly by carrying out the main part of the experimental work. I would especially like to thank Toni who worked with me from almost the beginning of the study and who, for example, conducted nearly all the wood resin analyses presented in this thesis.

Finally, I would like to give my wife my warmest thank who helped me in my work in every possible way as well as to our friends and our children who certainly make life worth living.

-To Ritva, Oona and Konsta-

Lappeenranta, May 2002

Jari Käyhkö

ABSTRACT

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The aim of this thesis was to produce information for the estimation of the flow balance of wood resin in mechanical pulping and to demonstrate the possibilities for improving the efficiency of deresination in practice.

It was observed that chemical changes in wood resin take place only during peroxide bleaching, a significant amount of water dispersed wood resin is retained in the pulp mat during dewatering and the amount of wood resin in the solid phase of the process filtrates is very small. On the basis of this information there exist three parameters related to behaviour of wood resin that determine the flow balance in the process:

1. The liberation of wood resin to the pulp water phase
2. The retention of water dispersed wood resin in dewatering
3. The proportion of wood resin degraded in the peroxide bleaching

The effect of different factors on these parameters was evaluated with the help of laboratory studies and a literature survey. Also, information related to the values of these parameters in existing processes was obtained in mill measurements.

With the help of this information, it was possible to evaluate the deresination efficiency and the effect of different factors on this efficiency in a pulping plant that produced low-freeness mechanical pulp. This evaluation showed that the wood resin content of mechanical pulp can be significantly decreased if there exists, in the process, a peroxide bleaching and subsequent washing stage. In the case of an optimal process configuration, as high as a 85 percent deresination efficiency seems to be possible with a water usage level of 8 m^3/o.d.t.

Keywords Mechanical pulp, Thermomechanical pulp, Wood resin, Extractives, Lipophilic extractives, Peroxide bleaching, Deresination, Washing.

UDC 676.15 : 676.021 : 676.054.1/.8

Contents

ABBREVIATIONS

CMC	Critical Micelle Concentration
CSF	Canadian Standard Freeness (Drainage Resistance)
CTMP	Chemithermomechanical pulp
DDJ	Dynamic drainage jar retention tester
EDTA	Ethylenediaminetetraacetic acid
FFA	Free fatty acids
GC	Gas chromatography
KCL	The Finnish Pulp and Paper Research Institute
LIGN	Lignans
LWC	Lightweight coated paper
MTBE	Methyl *tert.*-butyl ether
NF	Nanofiltration
NTU	Nephelometric turbidity units
o.d.	Oven-dried
PGW	Pressurised groundwood
RA	Resin acids
SE	Steryl esters
ST	Sterols
TG	Triglycerides
TMP	Thermomechanical pulp
TOC	Total organic carbon
UF	Ultrafiltration

1. INTRODUCTION

1.1 The Washing of Mechanical Pulp

The wood resin content of mechanical pulp has so far been a critical factor mainly in the production processes for food packing board grades. The current trend to minimise the consumption of fresh water and the washing of peroxide-bleached pulp have increased the importance and possibilities for decreasing the wood resin content in the production processes for printing paper grades as well. For example, in Finland nearly all paper mills using peroxide bleaching have recently installed or are planning to install the washing stage to their mechanical pulping plants.

Washing is carried out by installing an additional wash press, usually after peroxide bleaching, see Figure 1. In addition, the water circulation of the pulping plant and the paper machine are separated, some additional water is transferred to the pulping plant and the excess filtrate from the pulping plant is removed from the process.

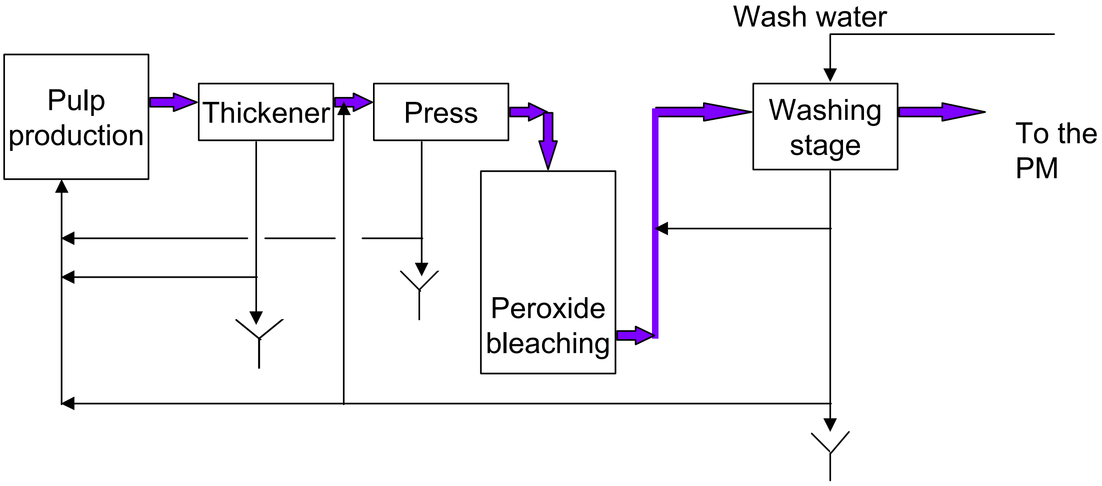


Figure 1. The washing of mechanical pulp.

1.2 The Effects of Wood Resin on the Product Quality and Runnability of the Paper Machine

Wood resin may have severe negative effects on the product quality and runnability of the paper machine. Wood resin may be deposited on process equipment, clog the pressing felts or stick onto drying cylinders, which results in holes and dark spots in the paper and web brakes [6]. The deposition problems have traditionally been controlled through the use of dispersing agents and fixatives and by avoiding process conditions that may enhance the agglomeration and deposition of wood resin [2]. The trend towards faster and more closed paper machines is making the deposition of wood resin a more important but also a more difficult problem to control.

Wood polymers dissolved from mechanical pulp have been found to decrease the agglomeration [59, 66] and stickiness [25] of wood resin and also to decrease the ability of wood resin to impair paper strength properties [54]. These wood polymers are removed from the pulp during washing much more extensively than is wood resin. This means that the washing of mechanical pulp may even increase the importance of decreasing the wood resin content of the final pulp.

The wood resin may impair the friction [11, 37], adsorption [35] and optical properties [13] of paper. In practice, probably the most important negative effect of wood resin on paper quality is the deterioration in strength properties [14, 54]. Wood resin has also been cited as lowering wet-web strength, the retention of fines and filler and causing foaming and corrosion. Also, the wood resin, more precisely the oxidised resin acids, may cause allergic reactions in humans [33]. In the case of food packaging board grades, the wood resin content of pulp is a critical parameter because of its tendency to cause taste and odour problems.

1.3 Wood Resin in the Mechanical Pulp

In the mechanical defibration process, the wood resin is dispersed to 0.1-1 µm colloids, see Figure 2, which are also assumed to be chemically homogeneous [10]. These colloids may exist freely in the water phase or adsorbed onto the fines and fibre material. Wood resin may exist also in the agglomerated form, as thin layers in the surface of fibres and encapsulated inside unbroken parenchyma cells [8]. At alkaline pH levels, the acidic wood resin, i.e. free fatty acids and resin acids, may exist in a dissolved form. It is also possible, that acidic wood resin components are adsorbed onto fibre material as single molecules. Probably, the main mechanism that governs the liberation of wood resin from mechanical pulp is the adsorption of wood resin colloids to the fibre material. The wood resin colloids that exist freely in the water phase can be retained in the pulp mat that is formed in dewatering.

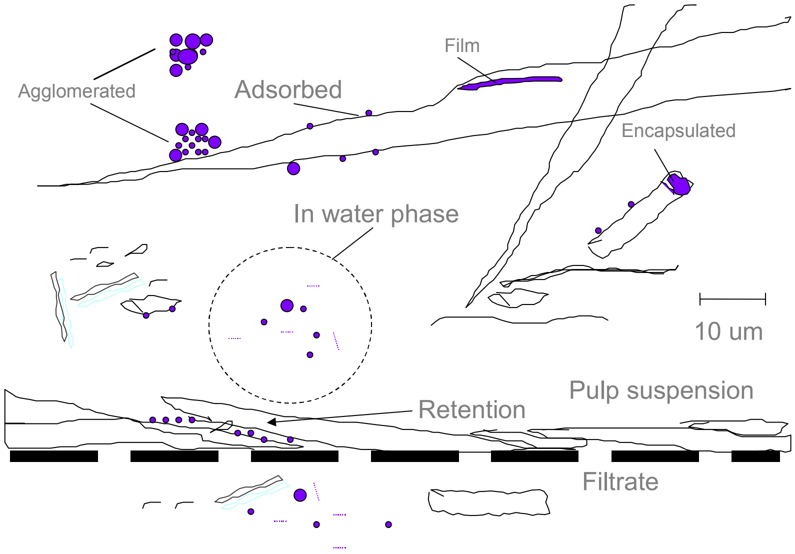


Figure 2. The physical form of wood resin in the pulp suspension.

Wood resin (lipophilic wood extractives, non-volatile wood resin) is a mixture of hundreds of different chemical substances. According to the analysis method used in this study [72], wood resin can be divided into five different main groups: free fatty acids, resin acids, sterols, steryl esters and triglycerides. These main groups have been shown to cover the major part, approximately 70 %, of the total wood resin in the case of Norwegian spruce [23]. Mechanical pulp also contains a complex mixture of numerous minor wood resin components. These components are ignored in this study but can be assumed to exhibit a behaviour in the process that is rather similar to that of the main wood resin groups.

1.4 The Objective and Structure of the Study

The deresination efficiency in mechanical pulp washing [1, 17, 19, 46, 29, 34, 51] and the behaviour of wood resin in mechanical pulp suspensions in laboratory [21,71], as well as in mill conditions [7, 15, 29, 38, 48] have been studied extensively. However, previous studies have not provided a complete understanding of the prediction of the deresination efficiency in existing processes.

The objective of this study was to identify the main mechanisms that influence the flow balance of wood resin in mechanical pulping and to show the possibilities for improving the deresination efficiency in practice.

In order to enable the analytical evaluation of deresination efficiency, it was assumed that there exist three parameters, related to the behaviour of wood resin, that determine the flow balance in the process:

1. The liberation of wood resin into the pulp water phase.
2. The retention of water-released wood resin in dewatering.
3. The proportion of wood resin degraded in peroxide bleaching.

The usability and accuracy of this classification in describing the flow balance of wood resin in the process was justified with the help of mill measurements.

The value and the quantitative effects of different process factors on these three parameters were evaluated based on mill measurements, laboratory studies and a literature survey. The parameter most extensively studied was the liberation of wood resin into the pulp water phase. The basic phenomena related to this liberation were also evaluated to some extent.

This information was used to briefly evaluate the deresination efficiency and the effect of different factors on deresination efficiency in a pulping plant that produces low-freeness mechanical pulp.

The study concentrated on the production of low-freeness TMP pulp made from Norway spruce, although the results are also applicable to the production of other types of mechanical pulp.

An important milestone in these studies was the introduction of a method to dewater the pulp sample. It was assumed that with this method, no dispersion of fibre-bound wood resin or retention of water-dispersed wood resin would occur during dewatering and hence, it would make it possible to measure the water-released wood resin content from pulp samples.

2. EXPERIMENTAL

2.1 Materials

The pulp samples used in the laboratory experiments and the labels used in the text were as follows:

TMP I: The sample was obtained from a Finnish news print mill after the second stage refiner with a consistency of 40 % and a freeness value of 160 ml.

TMP II: The sample was obtained from a Finnish LWC mill after the second refiner with a consistency of 45 % and a freeness value of 160 ml.

Pilot-TMP: Pulp samples with different freeness values produced with a KCL pilot refiner with a consistency of 27 % and freeness values between 100 and 250 ml. The pulp samples were made from the same homogeneous batch of wood chips.

After thorough mixing, the samples were stored at -24 °C until needed. The mill measurements were made mainly in the same mill from which the TMP II was obtained. Some measurements were also made in a Finnish ground wood plant that produces pulp for a folding box board machine. All the pulp samples were made from Norwegian spruce (Picea abies).

The chemicals used in the experiments are shown below:

Dilution:	Deionised water
pH level adjustment:	H_2SO_4 0.5 M
	NaOH 0.5 M
Electrolyte additions:	NaCl
	$CaCl_2$
	Alum, $AlK(SO_4)_2 \cdot 12\ H_2O$
Bleaching:	H_2O_2 (Finnish Peroxides Co)
	EDTA
	Sodium silicate, $2Na_2O \cdot 5SiO_2$, Ka. 43 % (Zeopol 25)
Lipase treatment:	Novo Resinase A, Activity 900 000 nkat/ml
Dispersing agents:	Fatty alcohol ethoxylate with HLB values 12 and 14 (Kemira Chemicals)
	Na-lauryl sulphonate (Kemira Chemicals)
	Lignosulphonate (Kemira)
	Condensed naphtalene sulphonate (Kemira Chemicals)
	Fennodispo 320 (Kemira Chemicals)

2.2 The Washing Procedure and Treatment of the Filtrate Sample

The washing procedure and treatment of the filtrate sample is illustrated in Figure 3.

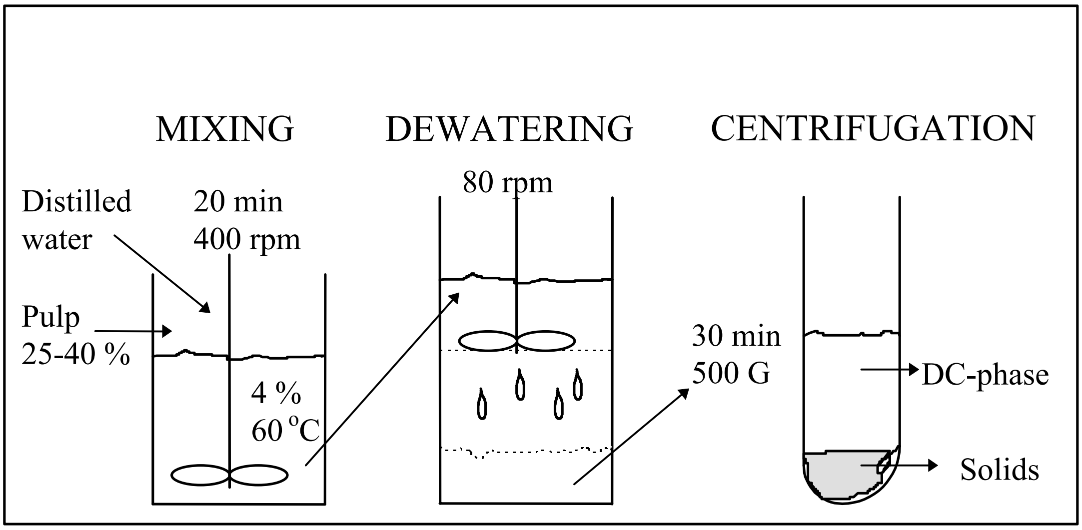


Figure 3. The washing procedure and treatment of the filtrate sample.

<u>The dilution and mixing of the pulp.</u> The pulp sample was diluted to 4-% consistency in deionised water and the resulting suspension (2.5 l) agitated at 60 °C for 20 minutes with the propeller rotating at 400 rpm. The specific power consumption during mixing in this case was 300 kW/o.d.t. It was assumed that these mixing conditions resemble rather well the average mixing that occurs in actual pulp production plants. Possible chemical additions were made at the beginning of the mixing. When lipase was used, 10-g/o.d.kg pulp was mixed gently to the pulp and pulp was left to stand for 10 minutes before mixing was started.

<u>Dewatering.</u> Immediately after mixing, 300 ml of the suspension was dewatered with a modified DDJ tester. The drainage filter used was a drilled metal plate with 1.5-mm holes. The suspension was agitated during dewatering with a propeller with a diameter of 9.5 cm and a rotational speed of 80 rpm. The propeller was located as close as possible (1-3 mm) to the surface of the metal plate. The amount of filtrate collected was 120 ml, and thus, the consistency of the pulp after dewatering was approximately 10 %. The aim of mixing was to prevent the wood resin from being retained in the pulp mat during dewatering. This was done in order as to obtain a representative picture of the amount of wood resin in the water phase in the pulp suspension. The traditional method for separating dissolved and colloidal substances is the direct centrifugation of the pulp slurry [66, 59]. The dewatering step was used because the direct centrifugation of pulp slurry with a higher consistency gives a smaller result compared to combined dewatering and centrifugation, see Figure 4. Probably, colloidal wood resin is retained in the pulp mat which is formed in the direct centrifugation of pulp slurry and the result obtained is then too small. In some experiments, dewatering was carried out with a laboratory-scale screw press similar to that used by Egenes and Helle [18].

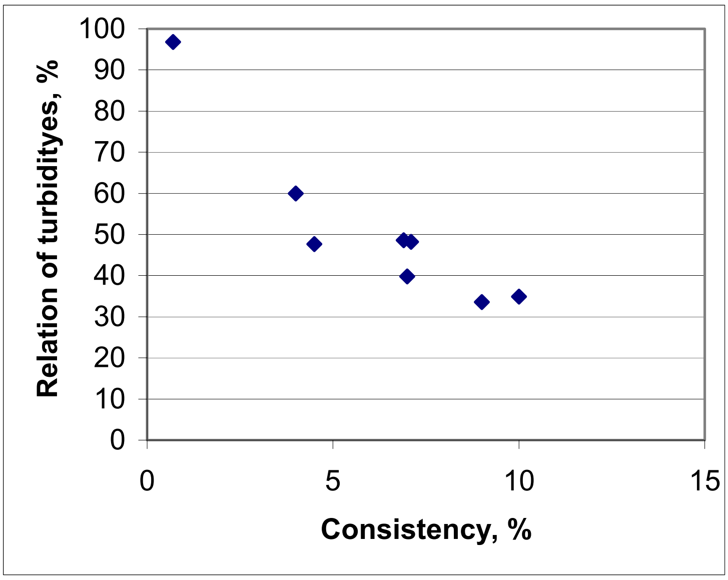


Figure 4. The turbidity from the directly centrifuged pulp slurry in relation to the turbidity when pulp slurry was dewatered before centrifugation. The direct centrifugation of pulp slurry gives smaller result compared to combined dewatering and centrifugation, especially with a higher consistency of pulp slurry.

The treatment of the filtrate sample. Immediately after dewatering, the filtrate was centrifuged (30 min, 500 g) and the supernatant pipetted for the analyses. The purpose of the centrifugation was to remove the solid material, which tended to disturb MTBE-extraction. The turbidity, measured after centrifugation, has also been observed to correlate very well with the concentration of wood resin [57, 62, 28, 56], which can also be seen in Figure 5. This has shown to be true especially when the system does not contain large amounts of other types of colloidal particles for example fillers.

The wood resin remaining in the supernatant after this dewatering and centrifugation treatment is referred in this text as dissolved and colloidal wood resin or water-released wood resin or wood resin in the pulp water phase.

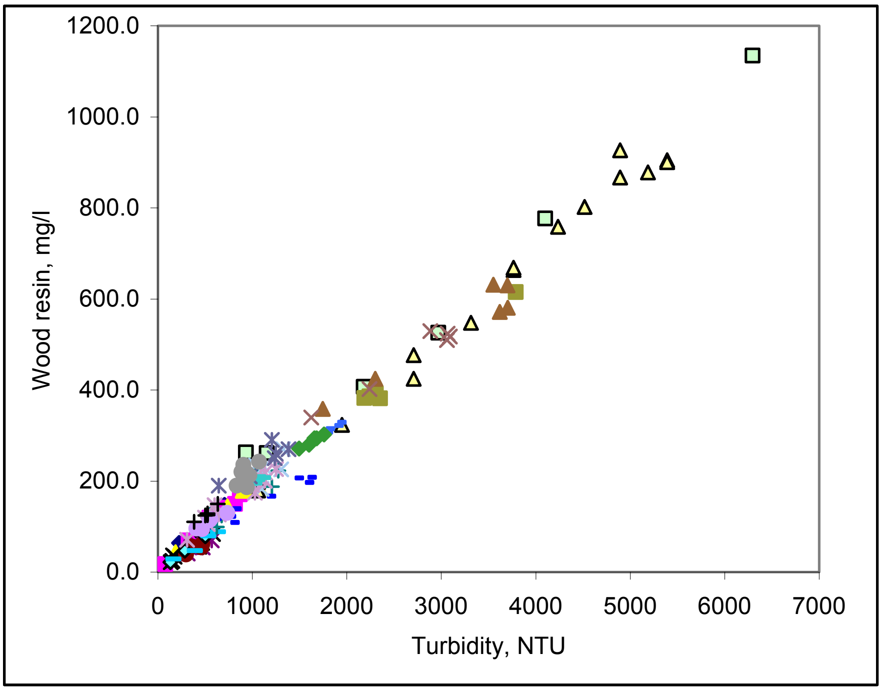


Figure 5. The correlation of turbidity and concentration of wood resin measured from the centrifuged water samples.

2.3 Determination of Retention and Proportion of Wood Resin in the Pulp Water Phase

The retention of water-released wood resin in dewatering was determined using Equation 1. In laboratory experiments, the filtrate was obtained by carrying out dewatering in a similar manner as was the basic treatment with the exception that there was no mixing and the suction pressure was 0.1 bar. In the mill measurements, the filtrate was obtained from the mill presses.

Equation 1. The calculation of retention values in dewatering:

$$R = 100 * \left(1 - \frac{c_f}{c_w}\right), \tag{1}$$

where

R retention, %,
c_f the concentration of wood resin in the filtrate, mg/l.
c_w the concentration of wood resin in the water phase of the feed pulp, mg/l.

The proportion of wood resin in the pulp water phase was calculated according to Equation 2.

Equation 2. The calculation of the proportion of wood resin in the pulp water phase.

$$X = 100 * \left(\frac{c_w * \left(\frac{100}{C} - 1 \right)}{c_p} \right), \qquad (2)$$

where

X the proportion of wood resin in the pulp water phase, %.
c_w the concentration of wood resin in the pulp water phase, mg/l.
c_p the concentration of wood resin in the pulp, mg/o.d.g.
C the consistency of the pulp, %.

2.4 The Methods Used in the Individual Experiments

Experiments related to the mixing time and intensity. A batch of the pulp was mixed at a certain speed and samples collected from it at different mixing times. Thereby, the volume being mixed decreased after each sampling. At the lower intensities, the pulp was mixed at 400 rpm for 15 seconds in the beginning and then for a specified time (15 seconds to 4 minutes) before sampling. The average power consumption for the different cases was evaluated based on these values. In the experiment carried out in the mill, the experimental conditions were similar to those in the laboratory experiments, except that the consistencies and temperatures during mixing were the same as in the sampled suspension. Also, in the cases where the consistency of the sample was above 4 %, the mixing speed had to be increased to ensure proper and even mixing. Additional mixing was started immediately after sampling.

pH tests. The pH level of the sample was adjusted by using sulphuric acid or sodium hydroxide, which were added to the dilution water, and the pH level was measured before dewatering.

Laboratory bleaching. The addition of chemicals and bleaching conditions are shown in the Table I. The chemicals were sprayed onto the pulp that was mixed by hand. EDTA was added half an hour before the other chemicals. After bleaching, the pulp which pH was about 8, was frozen without acidification. In the bleaching of lipase treated pulp, the lipase was mixed to the pulp for several hours at 60 °C before bleaching.

Table I. The bleaching chemicals and conditions

H_2O_2	3.5 %
EDTA	0.2 %
NaOH	2.5 %
Silicate	2.3 %
Temperature	60 °C
Time	2 h
Consistency	35 %

Whenever exceptions were made, they are brought forward in the text together with the results.

2.5 Analytical Procedures

The wood resin in the water samples was analysed based on a method described by Örså and Holmbom [72]. The wood resin from the solid samples were analysed by freeze-drying the sample, extracting it using a series extraction device (fexIKA 200 control) with a 9:1 acetone-water emulsion and then carrying out the rest of the analysis in the same way as for the water samples.

Turbidity was measured with a Hach 2100AN IS turbidimeter. In some cases, turbidity was used as a measure of the change in the concentration of wood resin in the filtrate. Turbidity measurement was made at room temperature at pH 5. The alkaline samples were acidified before measurement in order to precipitate the dissolved wood resin and, hence, improve the correlation between turbidity and concentration of wood resin

The TOC (total organic carbon) was measured with a Shimadzu TOC-5050 A carbon analyser.

The dissolved wood resin was obtained by filtering 2 ml of pulp through a filter with an average pore size of 0.1 µm (Gelman Science Supor-100).

The freeness measurement was performed according to the SCAN-M 4:65 standard.

3. THE SEPARATION OF WOOD RESIN IN WASHING

3.1 The Amount of Wood Resin in the Filtrate Solid Phase

Some earlier studies suggest that the concentration of wood resin in the solid phase of the filtrate, i.e. in the phase that is settled in the centrifugation, is slightly higher [36] or even significantly higher [48] than that in the solid phase of the pulp. In practical point of view this would mean that some wood resin, that does not exist in the pulp water phase, could be removed from the pulp in washing.

This phenomenon could arise from the fact that the proportion of fines in the solids of the filtrate is higher than that in the pulp. The amount of wood resin in the fines fraction of the pulp has been found to be considerably large than the amount in the other fractions of the pulp [30]. Also, this may be due to the adsorption of wood resin onto the solids in the white water system [48]. Especially when using pulp of a high freeness value and when dewatering is carried out with a screw press, the number of resinous parenchyma cells in the filtrate may be significant [19, 17] which should increase the concentration of wood resin in the solid phase of the filtrate.

In this study, the amount of wood resin in the solid phase of the filtrate samples obtained from different processes was found to be very small, see Table II. A similar result was also obtained in the filtrate recycling experiment carried out in the laboratory, see Figure 6.

Large amounts of wood resin were found only when the centrifugation of the filtrate was not carried out immediately after sampling, see Table II. This result shows that significant agglomeration or the adsorption of wood resin to the fibres and fines may occur in the filtrate and, thus, the centrifugation of filtrate should be carried out immediately after sampling.

Table II. The amount of wood resin in the solid phase of the filtrate when centrifugation was carried out immediately and several days after dewatering. In these cases, the amount of wood resin in the solids of the feed pulp was found to lie in the range of 3-8 mg/g.

Dewatering device	Pulp	Freeness	Wood resin in the solids, mg/g	
			Immediately	Few days delay
Screw press	GW	350	6	56
Laboratory screw press*	GW	350	5	-
Screw press	Bleached GW	350	8	-
Laboratory screw press*	Bleached GW	350	9	44
Roll press	PGW	140	-	25
Disk filter	TMP	80	4	-
Wire press	TMP	80	3	-
Wire press	bleached TMP	80	2	-

*The feed pulp from the mill press was dewatered with the laboratory screw press.

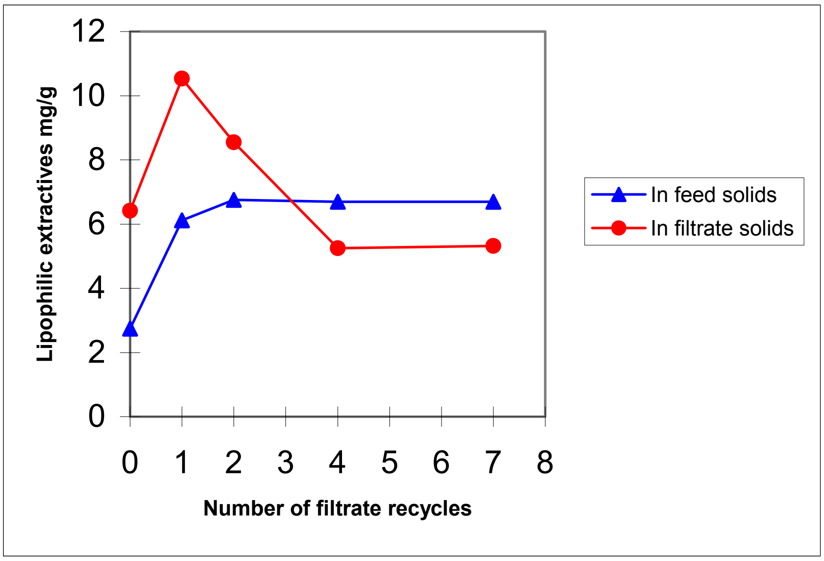


Figure 6. The amount of wood resin in the solids of the feed pulp and the filtrate in the filtrate recycling experiment carried out in the laboratory. Dewatering was carried out using a laboratory-scale screw press.

According to these results, it would seem that, in practice, the amount of wood resin in the solids of the filtrates does not differ significantly from that in the solids of the pulp and, hence, only the wood resin that exists in the water phase can be removed from pulp in dewatering. In order to have any practical influence on the deresination efficiency, the amount of wood resin in the solid phase of the filtrates should be many times higher than that observed in this study.

This result made it possible to distinguish three different basic phenomena or parameters that determine the flow balance of the of the wood resin in the process:
1. The proportion of wood resin liberated into the pulp water phase (or vice versa).
2. The retention of water-released wood resin in dewatering.
3. Proportion of wood resin that is chemically degraded in the process.

The second phenomenon is caused by the fact that part of water-released colloidal wood resin can be retained in the pulp mat that is formed during dewatering. Also, chemical changes of the wood resin in the process are known to occur, at least during the peroxide bleaching.

In this thesis, the effect of different factors on these three parameters was evaluated on the basis of laboratory studies and a literature survey. Also, information related to the values of these parameters in existing processes was obtained in the mill measurements. In addition to the fact that this division enables an analytical approach to be taken to this subject, this division and results obtained can also be directly used in computerised flow balance calculations.

3.2 The Behaviour of Wood Resin in a Pulping Plant

The behaviour of wood resin in a pulping plant was studied in the mill survey carried out in a TMP plant that produces LWC-grade pulp. The main target of this survey was to obtain information on the chemical and phase transitions that occur in the wood resin in the process. A Balas simulation model, which includes the most important connections, consistencies and flows, was elaborated on the basis of the process. The concentration of wood resin in the process was measured at different points and the behaviour of wood resin was calculated from these measurements.

The results presented here are based mainly on the study carried out in February 2000. In addition, measurements were also carried out on the same pulp production line in August 1998 and August 2000. The results obtained from these measurements are also presented in this context.

3.2.1 The Process Layout, Sampling and Analysis

The process lay out and sample points are shown in Figure 7.

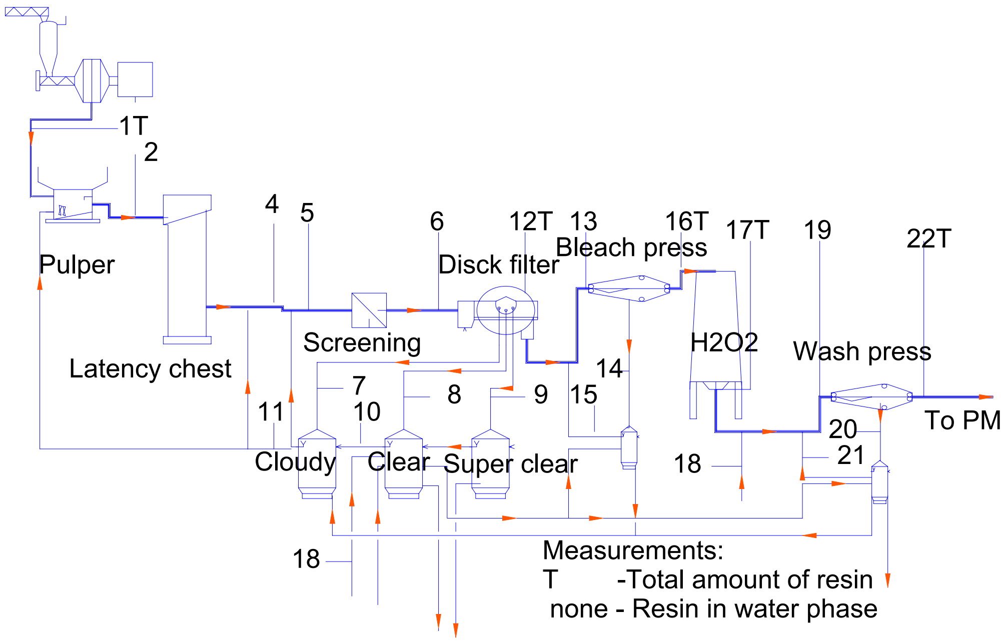


Figure 7. The process lay out, sample points and the analyses carried out in the mill study.

Four sample series, I to IV, were collected. The samples for the fourth series were collected only around the wash press. The turbidity, measured from the parallel samples, was quite similar, see Figure 8, and it, therefore, seems that the process was quite stable during sampling. In series III, sample points 15 and 19 differ clearly from the others, and the wood resin was not analysed at these points.

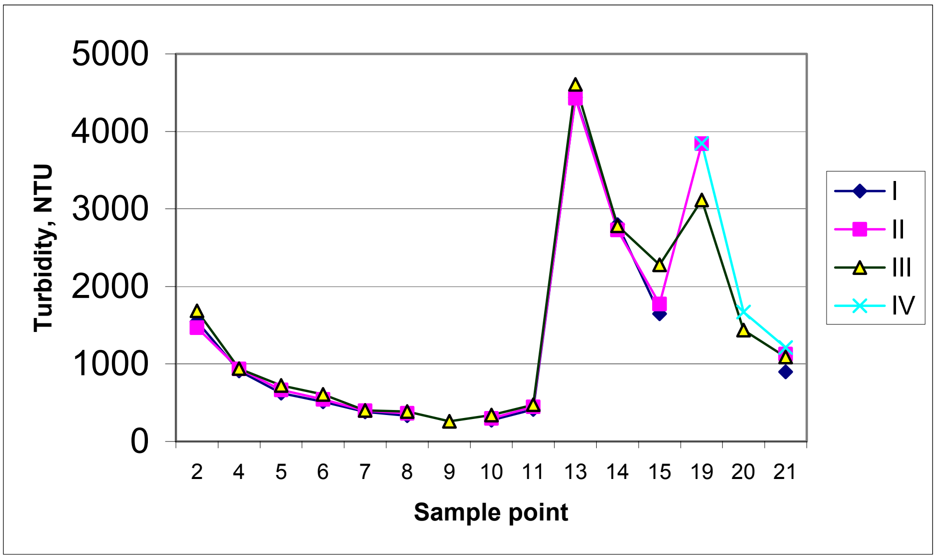


Figure 8. The turbidity measured from the samples.

The concentration of water-released wood resin was analysed from series II and from all the samples the number of which was between 13-21 (see Appendix 2). The average values were used in the mass-balance calculations.

Total amount of wood resin was analysed from series I and II (see Figure 9). In series I, the results are slightly higher compared to that of series II and this was mainly caused by the higher amount of triglycerides. Otherwise, the results obtained from series I and II are quite similar. In the calculation of mass balance, the results obtained from series II were used, because concentration of water-released wood resin was also measured mainly from series II.

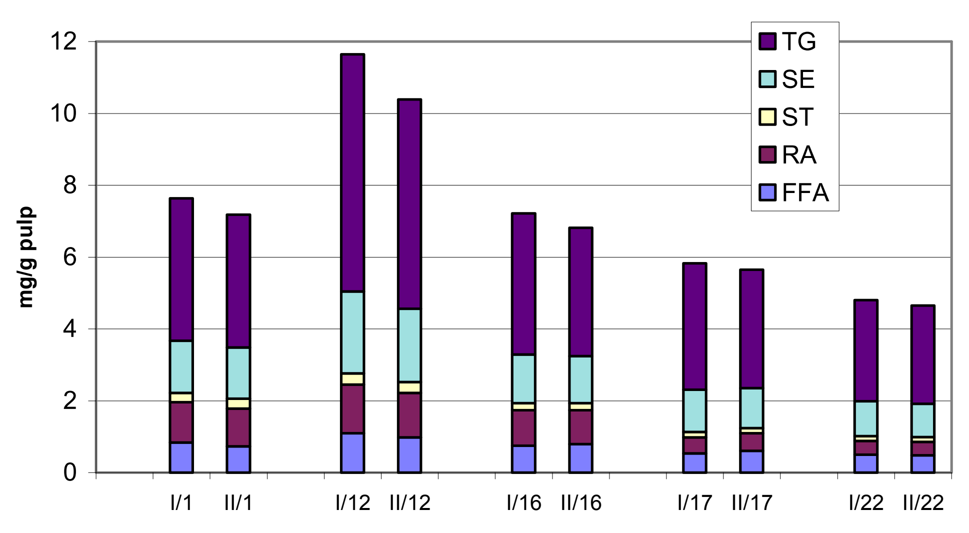


Figure 9. The total amount of wood resin measured at different points in the first and second sampling series.

The information related to the flows in the process was obtained from the mill process control system except for the shower water flows to the wire presses, which had to be measured separately. The consistencies were adjusted according to the consistency measurements made from series III. The supporting information was also obtained from routine measurements made by the mill laboratory. The flows and consistencies used in the mass balance calculation are presented in Appendix 1.

In the earlier measurement, the total amount of wood resin was measured in the pulp that came from the refiners only and the concentration of water-released wood resin at ten different points of the process. In the latest measurement, the total amount of wood resin was measured at two different points and the concentration of water-released wood resin at three different points in the process. The process information as well as the measured and calculated concentrations are presented in Appendix 4 and Appendix 5. In the case of the last measurement, the calculated values are not shown because the number of sampling points was so small that the measured and calculated values were exactly the same.

3.2.2 Modelling Principles

The calculation of the wood resin flow in the process using the Balas simulation software is based on following definitions:

- Wood resin exists in the simulation model only either in the dissolved or solid phase and the "dissolved phase" includes both the dissolved and colloidal wood resin. The behaviour of solid wood resin in the process follows that of the solid material, while dissolved wood resin behaves similarly to the water.
- The retention of water-released wood resin in dewatering is calculated in following way. The amount of dissolved wood resin, which leaves with the thick pulp, is increased by adjusting the retention value that maintains the ratio of the concentration of the dissolved wood resin in the feed pulp and filtrate at a constant level. The dewatering operation does not cause any phase changes in the resin. The additional dissolved resin, which follows the thick pulp, stays in the dissolved phase.
- Phase changes are carried out using reactors in which the desired proportion of wood resin is transferred from one phase to another.
- Degrading in bleaching is carried out in a reactor where an equal proportion of wood resin, both in the dissolved and solid phases, disappears.

The retention values in dewatering devices are directly obtained from measurements carried out on the wood resin in the water phase of the feed pulp and filtrate according to Equation 1. Degrading in bleaching is obtained from the measurements of the wood resin content carried out on the feed and outlet of peroxide bleaching. The phase change parameters are obtained by inserting suitable reactions, which carry out the desired phase change, into the simulation model. The values set for these reactors are adjusted so that the difference between the simulated and measured values is as small as possible.

3.2.3 The Behaviour of Wood Resin in the process

Figure 10 shows the description of the measurement points and the correspondence between the measured and calculated values, which is very good. This means that the reliability of the obtained parameter values is quite good and that no other significant chemical or phase changes occur in the wood resin in the process.

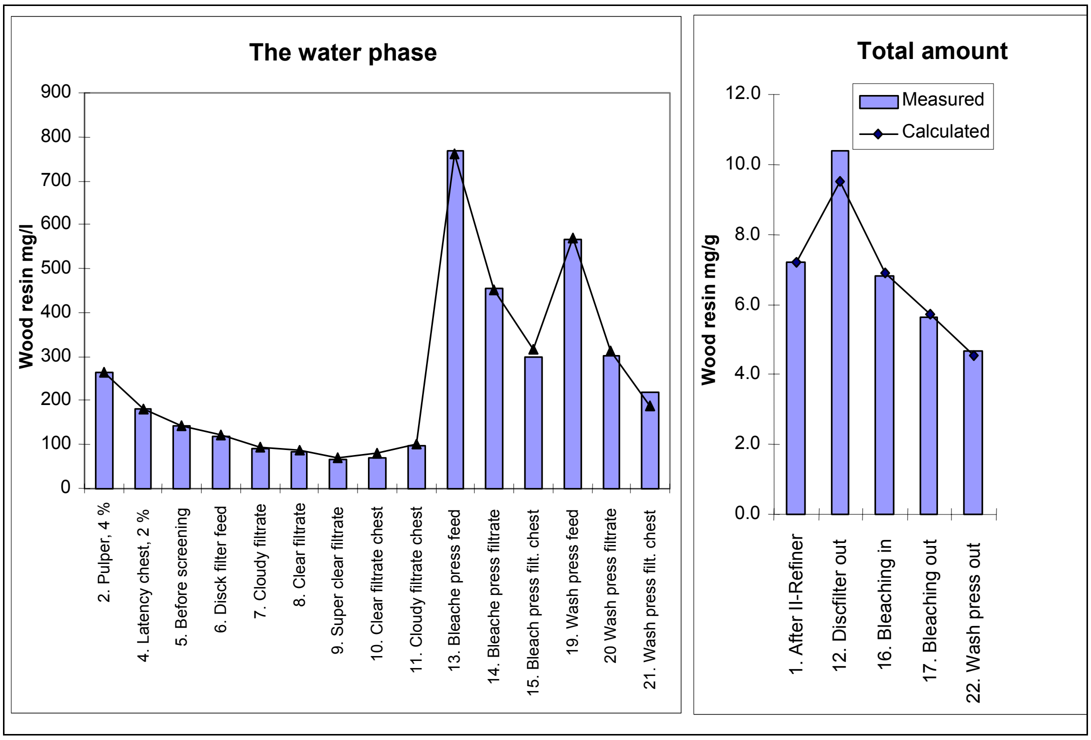


Figure 10. The correspondence between the measured and calculated values in the mill study.

The description and values of the obtained parameters can be seen in Figure 11:

- In the pulper after refining, 49 % of the wood resin was transferred to the water phase. After the latency chest, 15 % of the wood resin, which had not been transferred to the water phase in the pulper, was transferred to the water phase. This means that in the beginning of the process, altogether 56 % of the wood resin was transferred to the water phase.
- In the disc filter, the cloudy filtrate had the lowest and the super-clear filtrate the highest retention values. The overall retention value in the disk filter was about 27 %. In the bleach and wash presses, the retention value was about 40 %.
- During peroxide bleaching, 17 % of the wood resin was degraded, and after bleaching, 48 % of the fibre-bound wood resin was transferred to the water phase.

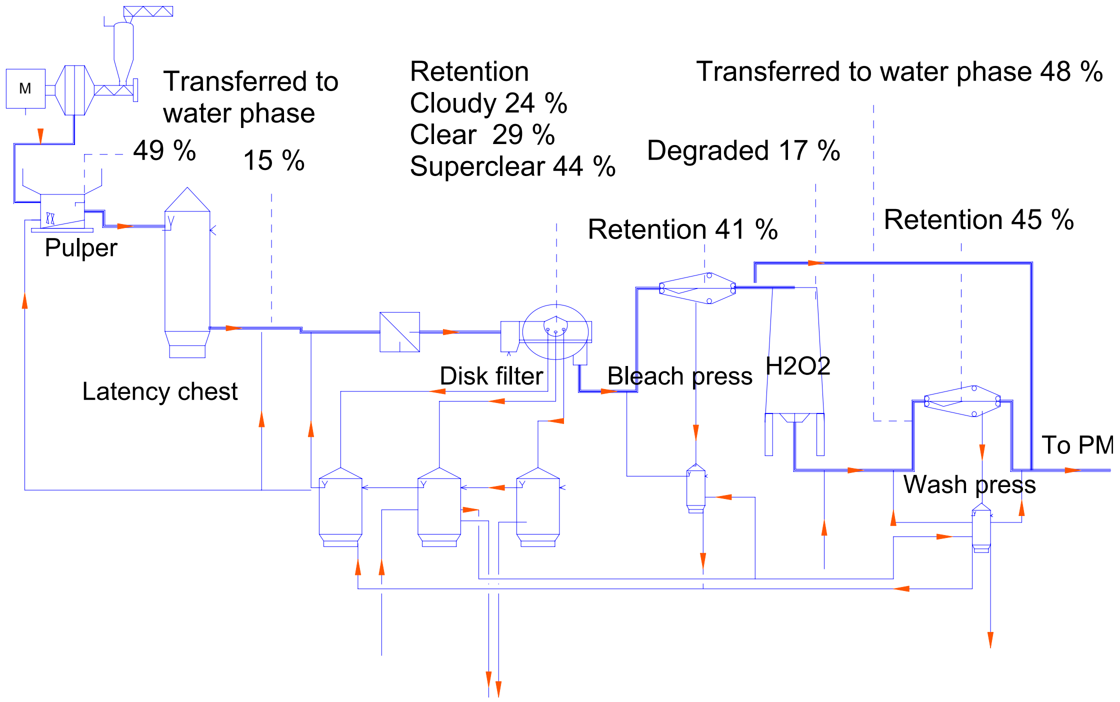


Figure 11. The behaviour of wood resin in the process.

Table III shows how turbidity, wood resin and different wood resin groups behave in the process. Appendix 3 shows the measured and calculated concentrations.

Table III. The behaviour of turbidity, wood resin and different wood resin groups in the process. TG: Triglycerides, SE: Steryl esters, FFA: Free fatty acids, RA: Resin acids, ST: Sterols, LIGN: Lignans. Lignans are water-soluble wood extractives and are not included in the wood resin.

	Parameters, %							
Description	**Turbidity**	**Wood resin**	TG	SE	FFA	RA	ST	LIGN
Transferred to water phase in the pulper	52	**49**	55	44	**37**	**46**	34	**36**
Transferred to water phase after the latency chest	0	**15**	19	15	15	**5**		
Retention, cloudy filtrate	29	**24**	25	22	30	27	8	0
Retention, clear filtrate	35	**29**	30	27	36	32	9	1
Retention, super-clear filtrate	45	**44**	47	39	49	49	10	1
Retention, bleach press	38	**41**	41	39	42	42	30	2
Retention, wash press	59	**45**	49	43	**43**	**24**	30	2
Degraded in the bleaching	0	**17**	**8**	**15**	**24**	**48**	25	**57**
Transferred to water phase after bleaching	54	**48**	58	52	**18**	**17**	35	**0**

Sterols seems to behave very differently in comparison to wood resin, see Table III, the reason being that a portion of lignans is detected as sterols in the analytical conditions used. The proportion of sterols in wood resin is very small, about 3 %, which means they do not have a significant effect on the observed behaviour of wood resin.

The most obvious differences in the behaviour of different wood resin groups can be seen in bleaching and post-bleaching, see Table III. The retention of resin acids in the wash press was about a half of that of the total wood resin. This indicates that about half of resin acids were in the dissolved form. Instead, the retention of fatty acids was very similar in comparison to that of neutral wood resin, triglycerides and steryl esters, and, therefore, only a small amount of fatty acids could exist in the dissolved form. The pH level in the wash press was 7.

The proportion of resin acids and triglycerides degraded in the bleaching is similar to that observed by Ekman et al. [22]. In the case of fatty acids, the observed degradation was much higher than that reported by Ekman et al. In addition, the proportion of fatty and resin acids transferred to the water phase after bleaching was clearly smaller when compared to that of neutral wood resin. One possible explanation for these results could be the formation of insoluble soaps with multivalent cationic metals such as, for instance, calcium or aluminium. If the dissolved fatty and resin acids form these soaps, they are most probably attached to the fibre material. Also, it is possible that these metal soaps are not leached from the pulp in the solid extraction [16] and, thus, are not included in the analysed wood resin.

The results from the earlier measurement carried out in August 1998 are presented in Table IV and those from the later measurement carried out in August 2000 in Table V. The number of sample points in these measurements was considerably smaller compared to that in the main survey. These measurements, after all, provide additional reference information related to the behaviour of wood resin in the process.

Table IV. The behaviour of turbidity, wood resin and different wood resin groups in the process based on the measurements carried out in August 1998. TG: Triglycerides, SE: Steryl esters, FFA: Free fatty acids, RA: Resin acids.

	Parameters					
Description	**Turbidity**	**Wood resin**	TG	SE	FFA	RA
Transferred to water phase in the pulper	**50**	**42**	50	**47**	**37**	**34**
Retention, cloudy filtrate	17	14	17	8	33	10
Retention, clear filtrate	21	17	17	13	18	21
Retention, super clear filtrate	40	26	29	20	28	27
Retention, bleach press	36	26	25	27	28	25
Retention, wash press	33	25	24	32	25	**11**
Degraded in the bleaching	**10**	**10**	5	**1**	**13**	**60**
Transferred to water phase after bleaching	**65**	**65**	**80**	**99**	**0**	**45**

When these two brief studies, see Table IV and Table V, are evaluated together with the main study, see Table III, the following similarities can be seen:

- In every case acidic wood resin (fatty and resin acids) was not liberated to the water phase after bleaching to same extent as neutral wood resin.
- In every case (Tables III-V), the proportion of acidic wood resin that changed over to the water phase at the beginning of the process is smaller compared to that of the neutral wood resin. This result is evaluated in chapter 5.1 together with similar results obtained in the multivariate experiments.

- In the first study (Table IV), the retention values are clearly smaller than those obtained in the later measurements (Table III and Table V). The reason for this is most probably the differences in the freeness value of the pulp. During the first measurement, the target freeness was 40 ml CSF and during later measurements 30 ml CSF.
- Also, these two brief studies showed the retention values of the different wood resin groups to be quite similar except for the retention of resin acids in the wash press, which was smaller in comparison to other wood resin groups. The last measurement (Table V) showed this difference to be smaller in comparison to the earlier measurements. In this case, the pH level in the wash press was also smaller (6) when compared to that obtained in the earlier measurements (7), which may explain the observed difference.
- The retention of turbidity-causing substances is clearly higher than the retention of wood resin, see Table III and Table IV. The particle size of colloidal wood resin has been shown to be about 0.1-2 µm [66, 42, 41] and it has been stated that wood resin colloids with a particle size of around 2 µm have the highest specific turbidity [10]. Hence, one possibility is that this difference is caused by the stronger retention of the larger wood resin colloids. In the pulp water phase, there also exists a large amount of so-called micro-fines that also cause some turbidity and may be related to this difference. These particles are larger in comparison to colloidal wood resin droplets and their shape is also elongated [39] as a result of which, the retention of these particles in dewatering should be higher compared to that of wood resin. The higher retention of turbidity-causing substances in comparison to that of wood resin could be then also related to the high retention of micro-fines.

Table V. The behaviour of wood resin and different wood resin groups in the process based on the measurements carried out in August 2000.

	Parameters				
Description	**Wood resin**	TG	SE	FFA	RA
Transferred to water phase in the pulper	**48**	**55**	**55**	**33**	**37**
Retention, disk filter	**29**	29	27	32	32
Retention, bleach press	**43**	42	42	42	44
Retention, wash press	**44**	45	45	45	**33**
Degraded in the bleaching	**12**	-6	7	20	45
Transferred to water phase after bleaching	**50**	**60**	**60**	**27**	**40**

3.3 The Behaviour of Wood Resin in Dewatering

The dewatering technique used for washing has shown to have a significant effect on the efficiency of deresination. The biggest difference is obtained if a shear type press (screw press) is compared to a mat-forming type press (wire press, roll press) [1, 46]. The reason for this difference is assumed to be that the retention of wood resin does not occur in the screw press, whereas in the mat-forming press it does. It has also been assumed that the screw press disperses fibre-bound wood resin [1].

Table VI contains the retention values measured from different mat-forming dewatering devices. The calculation of the overall retention is based on first-pass retention, feed consistency and the assumption that the discharge consistency is 100 %, with 10 m^3/o.d.t of the filtrate removed from the process and that the rest of the filtrate is used for the dilution of the feed pulp. In every case, the value of the overall retention is high, which means that the decreasing effect of retention on the efficiency of deresination is significant.

For example, the overall retention of wood resin in the disk filter was approximately 70 %, which means that even if all the wood resin in the pulp were in the water phase and the discharge consistency were 100 %, the deresination efficiency would still be reduced from 100 % to 30 % because of retention. This indicates that, due to retention, it is difficult to achieve efficient deresination in the disk filter.

Table VI. The retention of wood resin in mat-forming type dewatering devices.

Dewatering device	Feed consistency, %	First pass retention, %	Overall retention, %	Freeness, ml
Disk filter 1	0.67	**16**	**72**	40
Disk filter 1	0.6	**27**		30
Disk filter 2 [69]		**22**		30-50 (LWC)
Disk filter 2 [69]		**28**		30-50 (LWC)
Wire press 1	5	**10**	**17**	90
Wire press 2	5	**12**	**21**	90
Wire press 3	5	**21**	**34**	50
Wire press 4	3.5	**32**	**56**	50
Wire press 5	7	**26**	**32**	40
Wire press 5	9	**41**		30
Wire press 6	7	**25**		40
Wire press 6	9	**45**		30
Roll press 1	6	**41**	**51**	80
Roll press 2	6	**32**	**41**	80
Drum thickener		**4**		300

Some of these retention values are also shown in Figure 12, where it can be seen that the freeness value of the pulp has a significant effect on the retention of wood resin. At smaller freeness values, this effect becomes stronger.

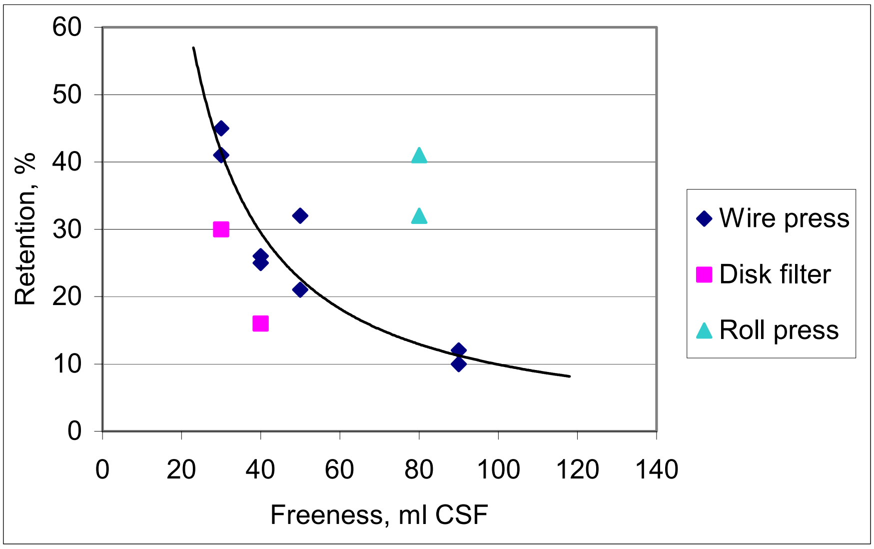


Figure 12. The retention of water-released wood resin vs. the drainability of the pulp.

The type of the dewatering device and the different factors determined in dewatering, for example the thickness of the pulp mat, feed consistency and dewatering speed, also probably have an effect on retention. The results shown in Figure 12 indicate that the retention in the roll press is higher and in the disk filter smaller in comparison to that in the wire press.

No retention of wood resin was observed in the screw press, see Figure 13. Instead, part of the fibre-bound wood resin was dispersed to the water phase. In the case of screw press 2, the concentration of wood resin in the filtrate strongly increased towards the discharge end of the press. Also, the concentration of wood resin in the screw press filtrate is clearly higher in comparison to the feed pulp water phase. In screw press 1, the dispersion of fibre-bound wood resin does not occur to a large extent nor does the mixing of that pulp release any of fibre-bound wood resin. This result shows that if wood resin can be liberated from the pulp by mixing, liberation will also occur to some extent during screw pressing.

The efficiency of this dispersion effect can be evaluated from the results obtained with screw press 2, see Figure 13. The amount of dispersion which occurred in the screw press was only 40 % of that which occurred in the mixing experiment. It is quite possible that retention of colloidal wood resin also occurred in the screw press when the consistency of the pulp increased in the screw barrel. Thus, the actual dispersion caused by the screw pressing may also be higher.

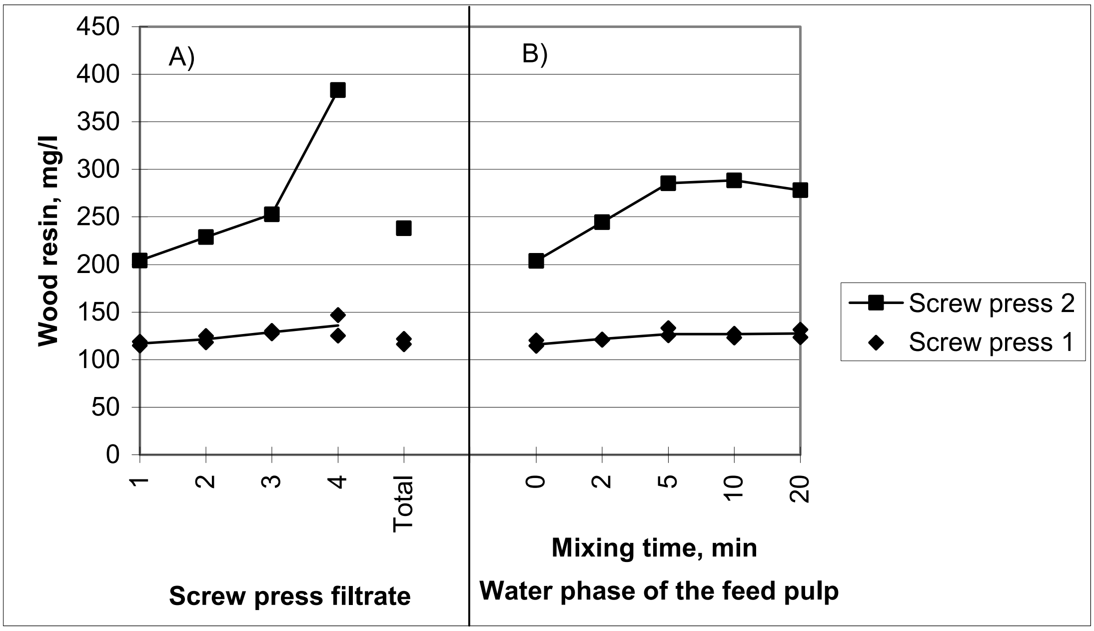


Figure 13. A) The amount of wood resin in the filtrates of the two screw presses (total) and in the filtrates obtained from different parts of the screw barrel (1-4). B) The amount of wood resin in the water phase of the feed pulp after the pulp has been mixed for a certain time (0-20 min). Screw press 2 was located in the process before and screw press 1 after peroxide bleaching. The freeness value of the pulp was approximately 350 ml.

4. THE INFLUENCE OF INDIVIDUAL WASHING VARIABLES

4.1 Mixing Time and Intensity

Earlier studies [4,8] have shown that the dispersion of wood resin in the pulp during mixing is a relatively slow process. It may take several hours before the concentration of wood resin in the water phase has stabilised. In these previous studies, the mixing intensity was quite low. At very high intensities, the dispersion of the wood resin occurs much more rapidly, see Figure 14. Less than one hour is needed for the complete dispersion of the wood resin. At these high intensities, from 300 to 4000 kW/o.d.t, dispersion occurs faster when the mixing intensity is increased, but the final level is the same.

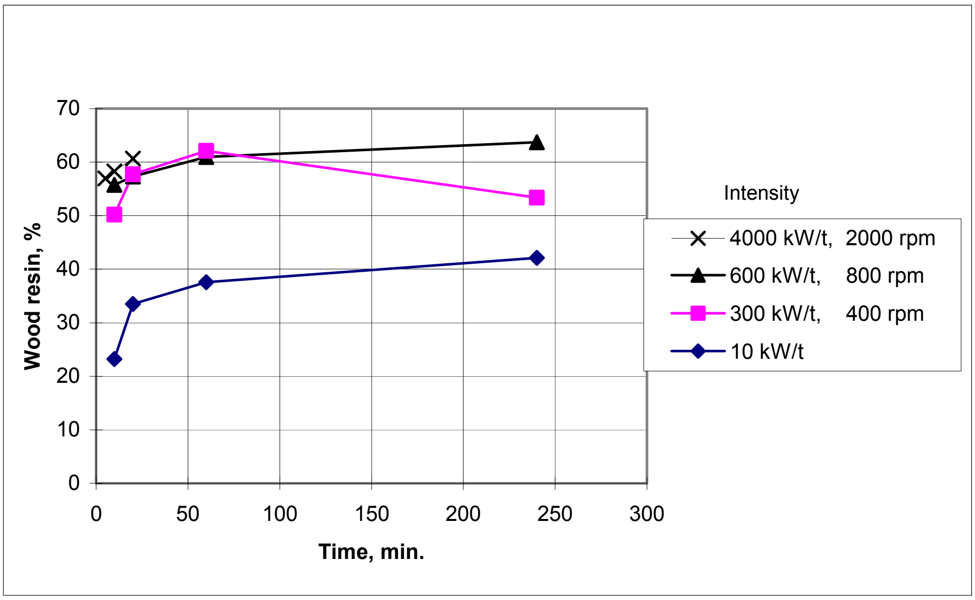


Figure 14. The effect of the mixing time and power on the proportion of wood resin in the pulp water phase, TMP I.

Two conclusions concerning the dispersion of wood resin in pulp at a high mixing intensity can be drawn from these results. Firstly, mixing intensity affects the speed of dispersion but not the level that is finally reached. Secondly, it is not possible to disperse all the wood resin in the pulp through an increase in the mixing intensity.

At lower mixing intensities, see Figure 14 and Figure 15, both the speed of dispersion as well as the level reached is strongly affected by the mixing intensity. Actually, without mixing, the amount of wood resin dispersed in pulp is very small, even for very long dwell times.

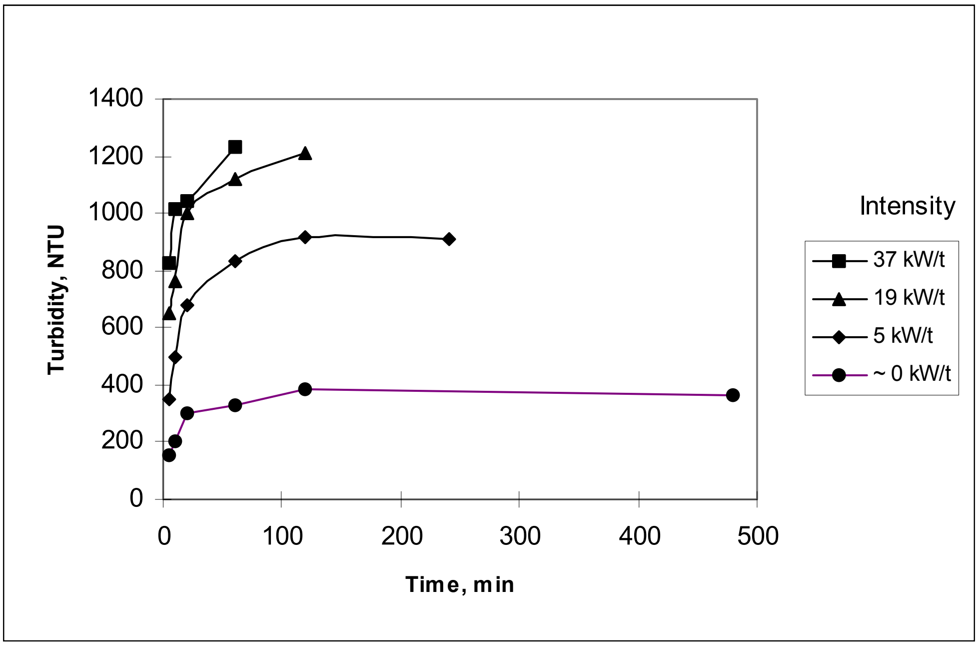


Figure 15. The effect of the mixing time and power on turbidity, i.e. on the amount of wood resin in the water phase, TMP I.

From a practical standpoint, the most important question is how efficient the mixing in the actual processes is and more precisely, is the mixing in the existing process sufficient to disperse all the wood resin in the pulp that is dispersible by mixing and if not, how much additional mixing increases dispersion. This was studied by mixing the samples taken from the process and measuring by how much the amount of wood resin in the water phase increased.

Figure 16 shows the process layout including sample points, significant dilution points, dwelling times and the energy consumption of the mixing equipment. Based on the laboratory results and information obtained from the process (Figure 14, Figure 15 and Figure 16), in this case, additional mixing should release the wood resin to the water phase in the samples taken from the process.

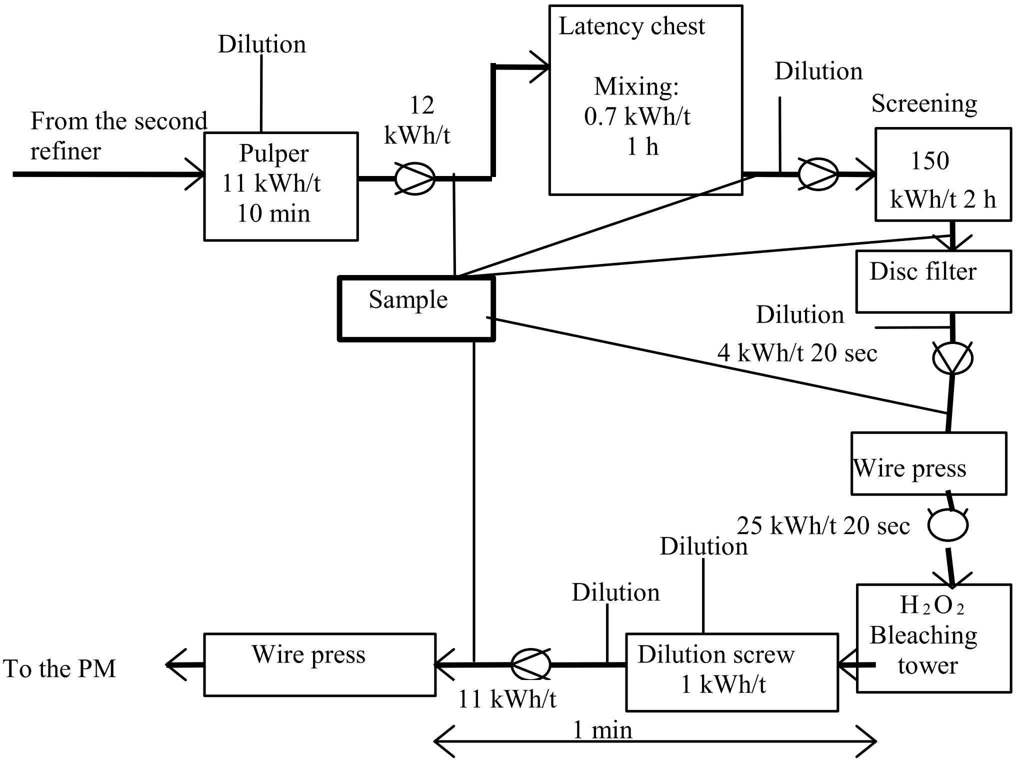


Figure 16. The process layout for the mill studies. The sample and dilution points, as well as the most important dwell times and specific energy consumptions are also shown.

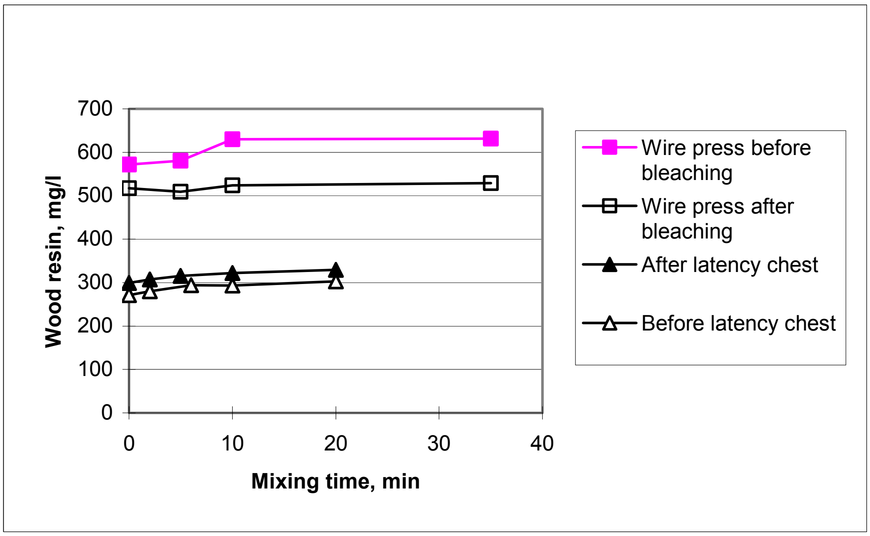


Figure 17. The effect of additional mixing on the amount of wood resin in the pulp water phase for different pulp samples.

Mixing lead to the liberation of wood resin to the pulp water phase in the samples taken before the latency chest, after the latency chest and from the press before bleaching, see Figure 17. This increasing effect seems to be quite small because the initial concentration of the wood resin in these samples was high. In the sample taken before the latency tower, additional mixing increased the amount of wood resin in the water phase by 30 mg/l and in the sample taken from the press before bleaching by 60 mg/l. The consistencies at these points were 4 and 7 %, respectively. The amount of wood resin in the pulp after refining was 6.3 g/kg. From these values, it can be calculated that additional mixing increased the amount of wood resin in the pulp water phase in both cases by 13 %-units. This is quite a significant value and these results show that, in this case, the mixing in the process was not adequate for the dispersion of wood resin from the pulp.

In the sample taken from the process after bleaching, additional mixing did not cause the liberation of wood resin to the water phase, see Figure 17. Very similar results in comparison to this mill measurement were obtained, also in the previous chapter, see Figure 13. Also in this case, mixing lead to the liberation of wood resin from the pulp taken from the process before bleaching but not from the sample taken after bleaching. The reason why additional mixing would liberate wood resin from unbleached but not from bleached pulp is not all that clear. One reason could be that the pulp was already quite efficiently mixed in the chemical mixer and between the bleach tower and wash press.

Mixing may also have a decreasing effect on the amount of wood resin in the water phase of the pulp. For longer mixing times, the amount of wood resin in the water phase was found to decrease, see Figure 18. Mixing alone did not cause this drop. The falling trend still continued after mixing had been stopped, albeit not as sharply as if the sample had been continuously mixed. Similar results were also observed with mill TMP, see Figure 19, but the decreasing effect was not as strong as in the case of pilot-TMP. The most probable reason for this is the agglomeration of colloidal wood resin. This phenomenon may have a reducing effect on the deresination if the dwelling time of the pulp in the process is considerably long or if this kind of phenomenon also occurs in the filtrates in the white water system.

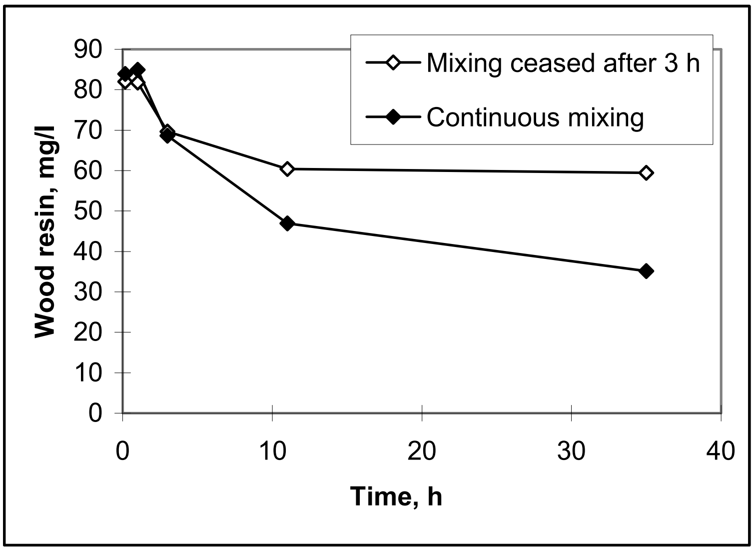


Figure 18. The effect of the mixing time on the amount of wood resin in the pulp water phase, Pilot-TMP.

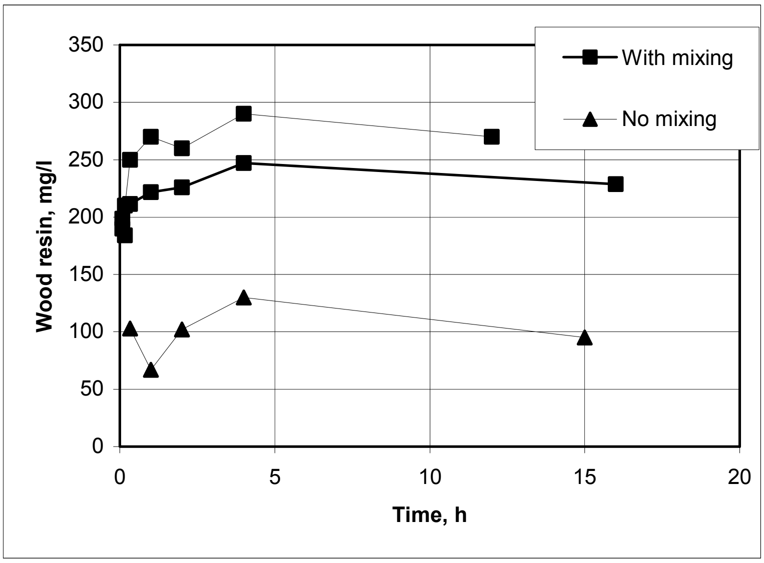


Figure 19. The effect of time on the amount of wood resin in the pulp water phase, TMP I.

4.2 Temperature

Experimental results of the effect of temperature on the liberation of wood resin from the pulp can be found in several studies. The effect has been mainly found to be positive [29, 34, 73], although there are also results according to which temperature has no effect [38, 70, 73]. Furthermore, Nylund [39] has observed that, when temperature is increased, the colloidal stability of wood resin may decrease. Therefore, under some circumstances, the effect of an increase in temperature on the amount of wood resin in the pulp water phase, might be even negative.

In our experiments, see Figure 20, the effect of temperature was clearly positive, although this effect weakens when the mixing time increases. It seems that at an increased temperature, wood resin is more easily liberated from the pulp, but that temperature does not affect the level reached when the pulp is extensively mixed. Chapter 4.1 concluded that the mixing in the process can be quite efficient and, thus, it is possible that the effect of temperature changes in the process on the liberation of wood resin to the pulp water phase can be quite small. The effect of temperature was studied further in the multivariate experiment, see Table XVI.

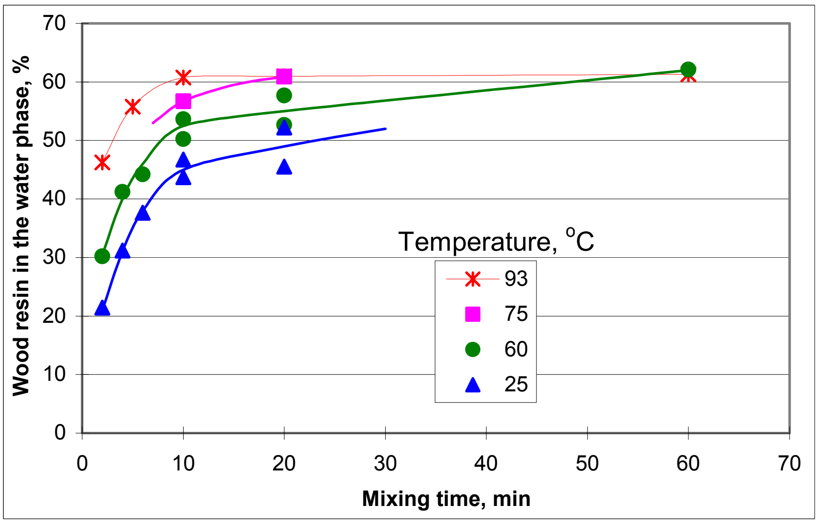


Figure 20. The effect of the mixing time and temperature on the proportion of wood resin in the pulp water phase, TMP I.

4.3 pH level

The pH level affects both the liberation of wood resin from pulp and the retention of wood resin in dewatering. The effect of the pH level on deresination efficiency has been studied extensively [1, 21, 29, 34, 38, 39] and the positive effect of an increase in the pH level is firmly established. At higher pH levels, the acidic wood resin is dissociated and, to some extent, dissolved. Also, it has been assumed that dissociated fatty and resin acids may act as emulsifiers, thereby promoting the dispersion of neutral wood resin into water [71].

In Figure 21, it can be seen that the strongest effect of the pH level on the liberation of wood resin is obtained when the pH level is below 5. This increase is difficult to explain by the dissociation of acidic wood resin since the pKa values of the fatty and resin acids are about 5.5-6.5 [68]. Nylund [40] observed that the pKa value for the colloidal matter obtained from mechanical pulp was below 4. He assumed that this was caused by the adsorption of acidic wood polymers onto the surface of the wood resin colloids. Also, the fibre material contains similar acidic wood polymers which are dissociated when the pH level is increased and, hence, that increase the anionic charge of fibre material [30]. The effect of the pH level on the liberation of wood resin into the pulp water phase is, thus, very probably also related to the dissociation of these wood polymers and the effect of this dissociation on the anionic charge of colloidal wood resin and fibre material.

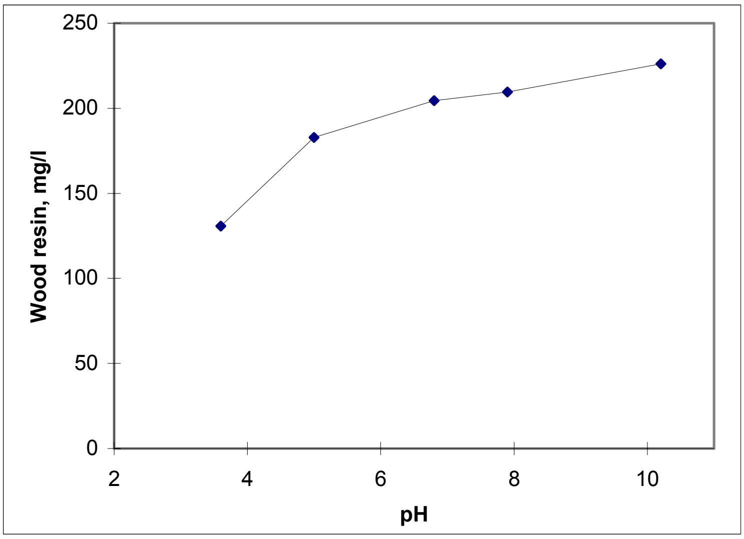


Figure 21. The effect of the pH level on the amount of wood resin in the pulp water phase, TMP I.

Clear differences can be seen in the behaviour of different wood resin groups, Figure 22. The amount of acidic wood resin increases throughout the whole pH spectrum studied, but the amount of neutral wood resin does not change considerably in the region where the pH level is above five. This difference is caused mainly by the dissolution of free fatty acids and resin acids, see Figure 23.

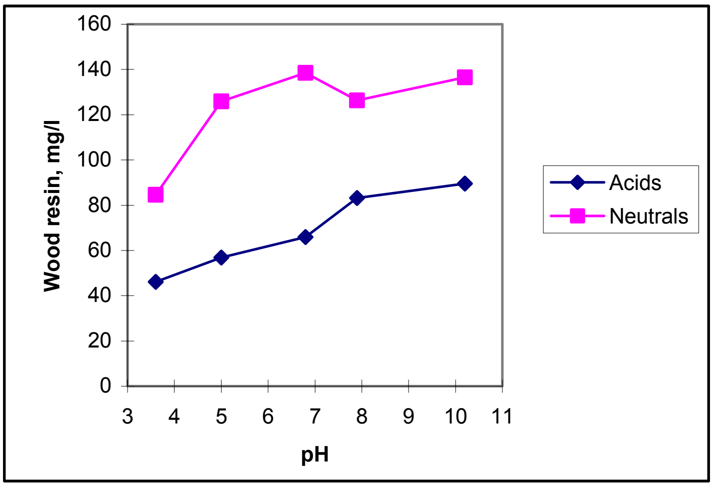


Figure 22. The effect of the pH level on the amount of acidic (fatty acids and resin acids) and neutral (sterols, steryl esters and triglycerides) wood resin in the water phase, TMP I.

The dissolution of acidic wood resin begin after the pH level has exceeded 7. The amount of resin acids and free fatty acids in the pulp were approximately the same, but the amount of dissolved resin acids is much higher compared to that of dissolved free fatty acids, see Figure 23. In the mill measurements, shown earlier on in this thesis, the resin acids were also dissolved to a higher extent because their retention in the wash press was clearly smaller compared to that of fatty acids, see Chapter 3.2.3. Similar results have also been obtained in the other studies [21, 68], which show that resin acids are dissolved much more easily in comparison to fatty acids.

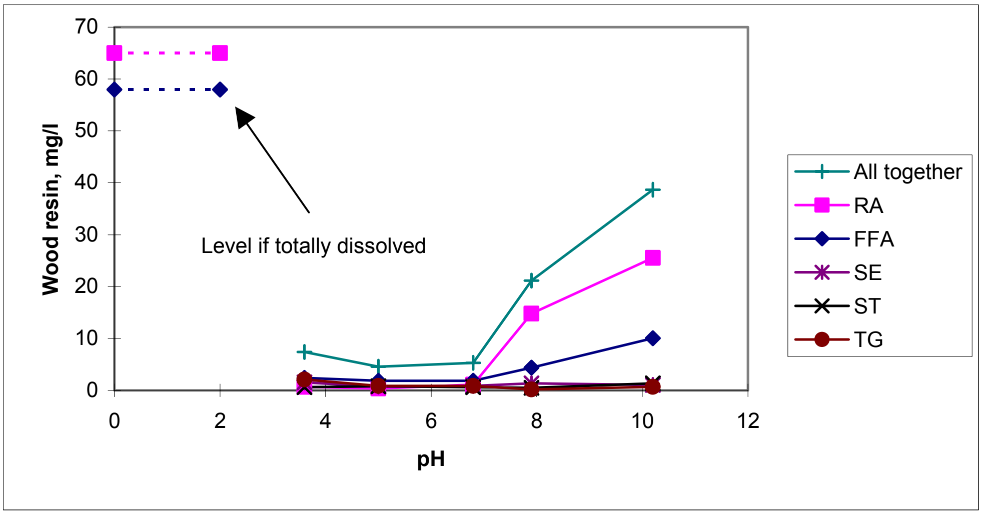


Figure 23. The effect of the pH level on the amount of dissolved wood resin, TMP I.

The effect of the pH level on the retention of wood resin can be seen in Figure 24. It can be observed that the pH level does not affect the retention of neutral wood resin, whereas the retention of acidic wood resin decreases rather linearly when the pH level is increased. At a pH level of 8 and above, this drop can be explained by the dissolution of the acidic wood resin, see Figure 23, but at lower pH levels, the reason for this drop remains unclear.

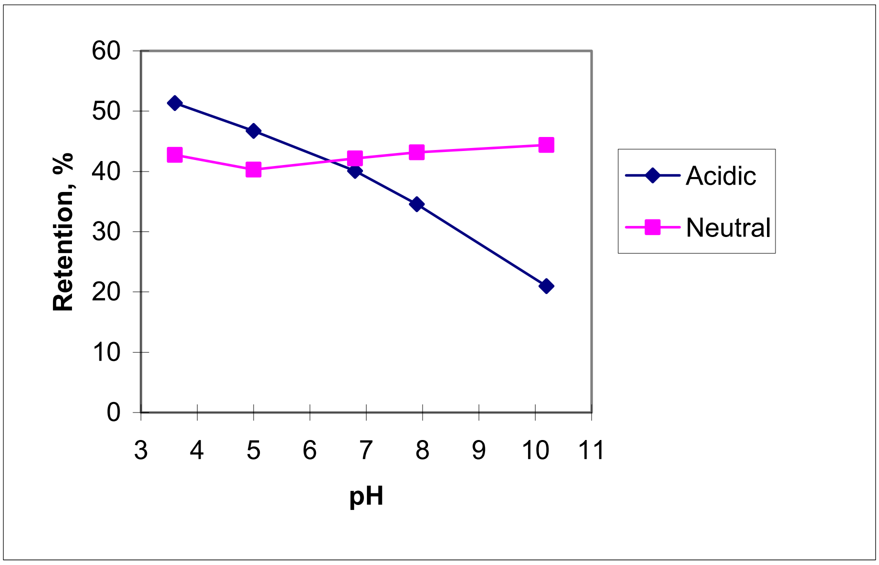


Figure 24. The effect of the pH level on the retention of water-released wood resin in dewatering, TMP I.

The effect of the pH level on the amount of wood resin in the filtrate in different studies, as well as information related to the respective experimental conditions, is shown in Table VII. Even thought the fact that the experimental conditions and pulps used in these studies differ considerably from each other cause the comparability of the information in Table VII to suffer, the overall effect of the pH level on the wood resin is clear.

Table VII. The effect of the pH level on the amount of wood resin in the filtrates in different studies.

Study	pH region	Amount in the filtrate/total amount at lower pH levels, %	Amount in the filtrate/total amount at higher pH levels, %	Difference	Acidic wood resin/total amount, %	Retention of wood resin in the thickening	Mixing before thickening
[53]	5-8	6	33	27	pine*	yes	no
[34]	5-8	17	44	27	pine*	yes	low
[29]	5-8	25	39	14	-	yes	moderate
[38]	5-8	20	35	15	pine*	yes	low
[1]	5-8	61	73	12	pine*	no	effective
[21]	5.5-8	35 55	53 71	18 16	55	yes no	effective effective
this study	5-8	28 55	40 65	12 10	38	yes no	effective effective

* The amount of resin acids in pine is large, so the proportion of acidic wood resin to the total amount should be very high.

In mechanical pulp washing, the pH level may vary in the range of approximately between 5 and 8. In Table VII, the effect of the pH level on the amount of wood resin in the water phase in this area differs considerably; namely, from 10 % to 27 %. The most significant effects were obtained in the cases where the amount of wood resin at a lower pH level was very small [34,53]. These studies probably do not provide a quantitatively correct picture of the effect of the pH level in the existing washing processes.

In light of these results, it can be said that a change in the level of the pH level from 5 to 8 increases the amount of wood resin in the pulp filtrate by no more than 10-18 percentage units for a single dewatering under mill conditions [1, 21, 29, 38]. Hence, it can be concluded that the adjustment of pH level alone can be a fairly weak means of improving the deresination efficiency of mechanical pulp, even if it has a clear influence on the behaviour of wood resin.

4.4 The Use of Lipase

4.4.1 Introduction

The use of lipase makes it possible to study the effects of the composition of wood resin in order to understand its behaviour without changing other properties of the pulp. In fresh Norwegian spruce, the proportion of free fatty acids in the wood resin is very small, about 10 %, and the proportion of triglycerides about 50 %. The proportion of acidic wood resin increases greatly when the triglycerides are hydrolysed to free fatty acids in lipase treatment. This could have a significant effect on the behaviour of the wood resin, as was mentioned at the beginning of the previous chapter.

The composition of wood resin in the process may vary considerably depending on the wood species used, the sapwood/heartwood ratio and wood storage [20]. Also, lipase treatment is reported to be in use in mill scale [27] in order to reduce the deposition problems caused by wood resin.

The aim of the present study was to obtain the answers to two questions. Firstly, how does the composition of wood resin affect the liberation of wood resin to the pulp water phase and secondly, could it be possible to improve the efficiency of deresination in practice with lipase treatment?

4.4.2 The Accuracy of the GC-Analysis Method

One critical point, when studying the effects of lipase treatment, is the GC analysis of the wood resin. If the result is not correct for the free fatty acids and triglycerides, lipase treatment may alter the amount of wood resin being analysed, even if the real amount of wood resin is the same. A possible error in the analysis was studied by treating two different water samples with lipase and carrying out three parallel analyses, both from the lipase-treated as well as the untreated samples.

About half of the wood resin consisted of triglycerides which were totally hydrolysed to free fatty acids in the lipase treatment, see Figure 25 and Figure 26. The amount of free fatty acids that was formed should have been about 4 % smaller because of the cleavage of glycerol from the triglyceride molecule. This should have decreased the amount of wood resin by about 2 %. On the other hand, the pulp also contains small amounts of mono- and diglycerides, which are about 1-2 % of the total amount of wood resin and which were not detected as such in the analysis of the wood resin. The possible hydrolysis of these mono- and diglycerides may increase the amount of free fatty acids by approximately the same amount as that by which glycerol is released from the triglycerides and, hence, the total amount of wood resin analysed from the lipase-treated and untreated sample should be the same.

In the first comparison (Figure 25) the amount of wood resin in the lipase-treated sample was about 4 % higher and in the second comparison (Figure 26) about 4 % lower in comparison to the untreated sample. These observed differences are contrary to each other and so insignificant that it can be assumed that in the analysis, no systematic error exists between any of the lipase-treated and the untreated samples.

In both cases, lipase treatment increased the amount of resin acids. This is because some very-long-chain fatty acids that were liberated in the triglyceride hydrolysis, exist in the same region of the gas chromatogram as do the resin acids, as a result of which they are detected as resin acids. Two examples of these kinds of fatty acids are eicosatrienoic acid (20:3) and eicosanoic acid (20:0) [23].

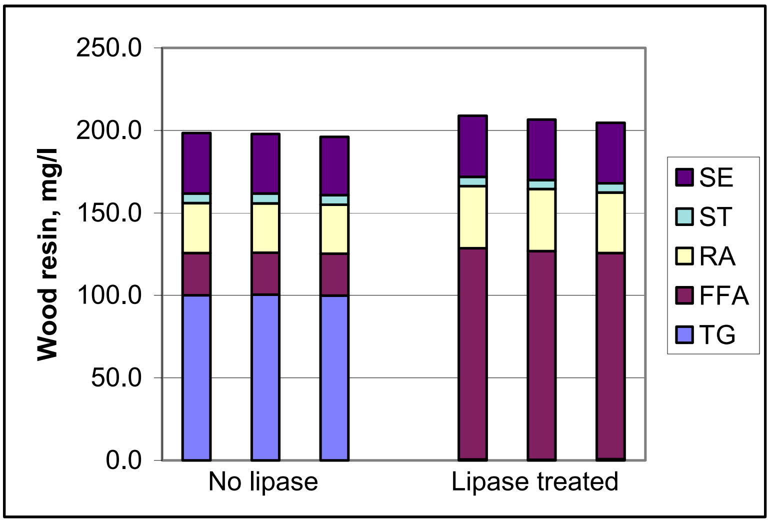


Figure 25. The effect of lipase treatment on the amount of wood resin analysed. The water sample was prepared using TMP I.

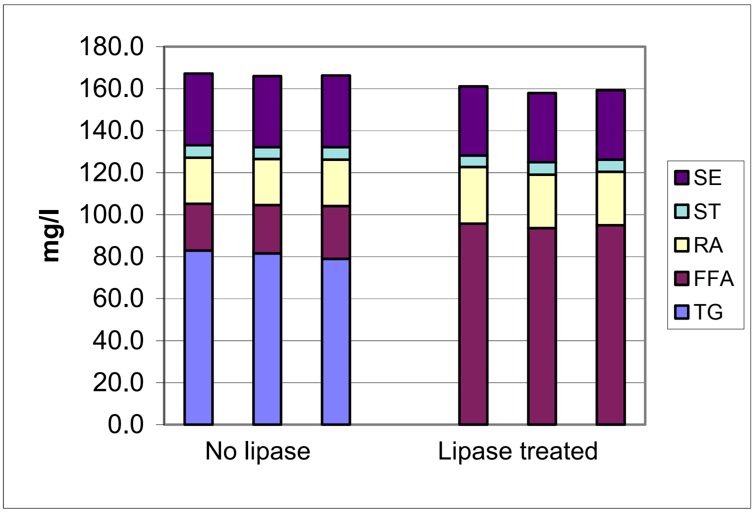


Figure 26. The effect of lipase treatment on the amount of wood resin analysed. The water sample was prepared using TMP II.

4.4.3 Results

In the experiments carried out with TMP I, lipase treatment did not have any effect on the amount of wood resin in the pulp water phase in whole pH region studied, see Figure 27.

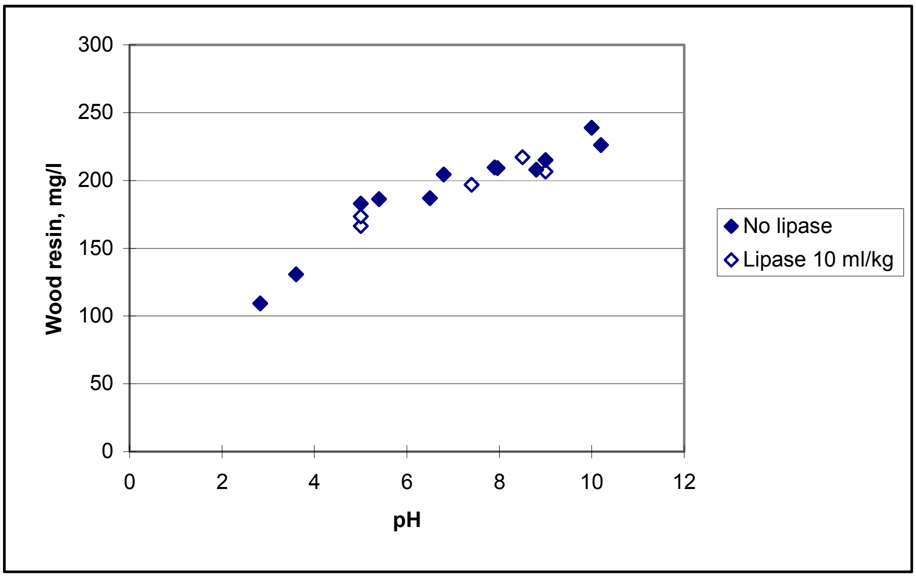


Figure 27. The effect of lipase treatment on the amount of wood resin in the pulp water phase with TMP I.

The effect of the lipase quantity on the amount of wood resin in the pulp water phase and on the amount of dissolved wood resin was studied further with peroxide-bleached pulp and unbleached TMP II pulp. These experiments were carried out at elevated pH. For both pulp samples, the usage of lipase slightly decreased the amount of wood resin in the pulp water phase, see Figure 28 and Figure 29.

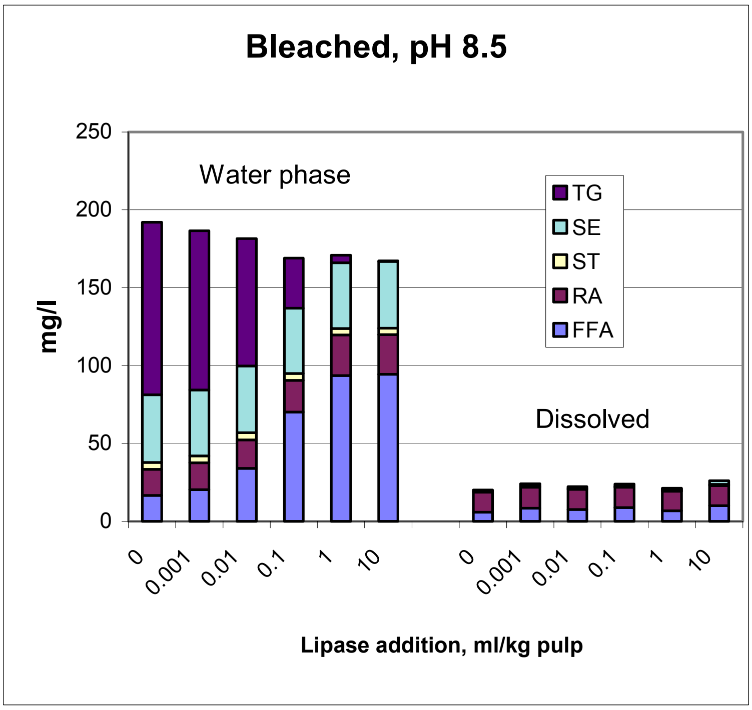


Figure 28. The effect of the addition of lipase on the dissolution and liberation of wood resin to the pulp water phase. The pulp was obtained from the discharge of the wash press during the mill measurement presented in Chapter 3.2.

Besides affecting the behaviour of wood resin through the hydrolysis of triglycerides, it is possible that lipase addition may also have an affect via another mechanism. Lipase molecules probably have both hydrophilic and lipophilic properties, because it is miscible to the water but while it can totally hydrolyse triglycerides, it should also be able to penetrate wood resin colloids. The lipase molecule may also then bear some surface-active properties and when adsorbed onto the surface of wood resin colloids or fibre material, may cause some changes in the behaviour of the wood resin. For example, it has been shown that Resinase lipase can be almost totally adsorbed onto the pulp material [24].

In Figure 28, it can be seen that the negative effect of lipase addition becomes more severe when the rate of addition increases. This negative effect seems to be more proportional to the progress of the triglyceride hydrolysis than to the increase in lipase addition. At the three biggest addition points, where the hydrolysis of triglycerides is already complete, the amount of wood resin in the pulp water phase does not decrease, even when the rate of addition of lipase increases from 0.1 to 10 ml/kg. Therefore, it seems that this negative effect is caused by the more complete hydrolysis of the triglycerides and not from the presence of lipase in the pulp.

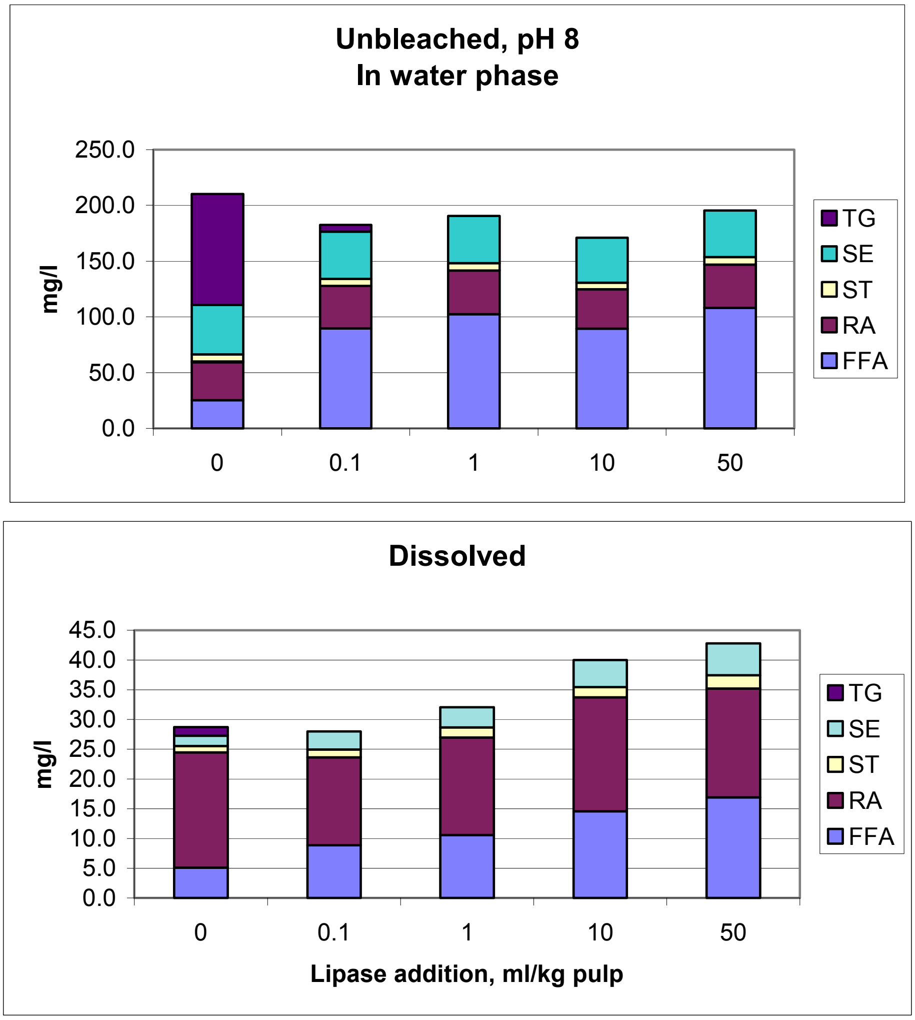


Figure 29. The effect of the addition of lipase on the dissolution and liberation of wood resin to the pulp water phase for TMP II pulp.

For bleached pulp, lipase addition does not affect the amount of dissolved wood resin, whereas for unbleached pulp it has a clear increasing effect, see Figure 29. The amount of dissolved steryl esters and sterols increases clearly although they should not exist in the dissolved form under these conditions. The dissolved substances were obtained by filtering the sample through a filter with an average pore size of 0.1 µm. The smallest wood resin colloids can pass through the filter, which explains the presence of neutral wood resin in the dissolved fraction. The increase of the "dissolved" wood resin observed in here is probably caused by the decrease in the particle size of wood resin colloids. The hydrolysis of the triglycerides is quite complete already at the lowest addition level, but the amount of "dissolved" wood resin increases considerably when the rate of addition of lipase increases. This indicates that the decrease in the particle size of wood resin is not caused by the hydrolysis of the triglycerides but by the presence of lipase in the pulp.

It is possible that the use of lipase could have a increasing effect on the release of wood resin from the pulp in a situation in which the amount of wood resin in the pulp is so low that a significant proportion of wood resin could exist in the dissolved form. In practice, this sort of a situation could exist at the end of multistage washing when the pH level is high such as is the case, for example, in the production of folding boxboard. This kind of a situation was studied by adding lipase to the pulp at a low consistency, see Figure 30. At 1-% consistency, the use of lipase increases the amount of "dissolved" wood resin, but the total amount of wood resin liberated from the pulp still remains at a clearly lower level in comparison to that of the untreated pulp.

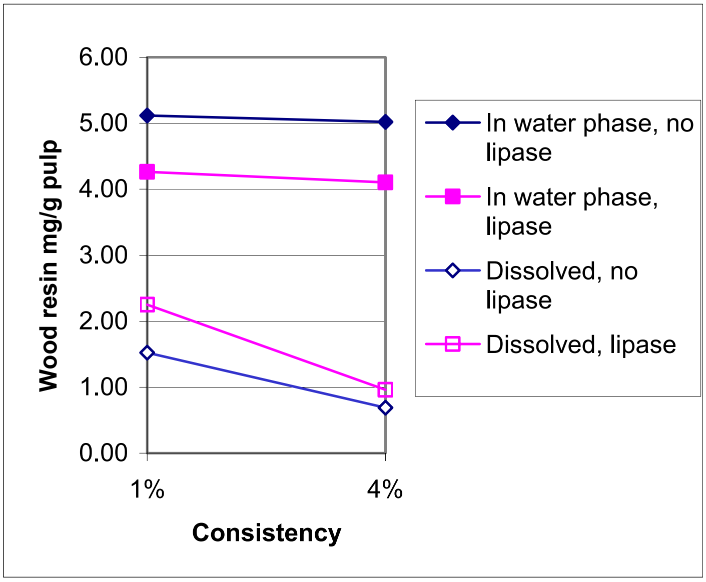


Figure 30. The effect of lipase treatment on the amount of wood resin in the pulp water phase and dissolved wood resin for unbleached pulp at different consistencies. The lipase addition was 10 ml/kg, pH 8 and the wood resin content of the pulp 7.2 mg/g pulp, TMP II.

Figure 31 shows that the concentration of the dissolved free fatty acids remains quite constant even though the consistency of the pulp decreases from 4 to 1 % and it would, therefore, seem that the amount of the free fatty acids in the pulp does not determine the rate of dissolution. The amount of dissolved resin acids, on the other hand, clearly falls because at 1-% consistency, nearly all the resin acids in the pulp exist in the dissolved form. If the wood resin content of the pulp had been very low, smaller than 0.5 kg/o.d.t, a significant part of the free fatty acids might exist in the dissolved form and the usage of lipase could increase the rate of dissolution and, hence, liberate the wood resin from the pulp. Increasing the pH level above 8 would further improve the situation, see Figure 23, although this is probably not possible in practice because of the danger for the alkaline darkening of the mechanical pulp.

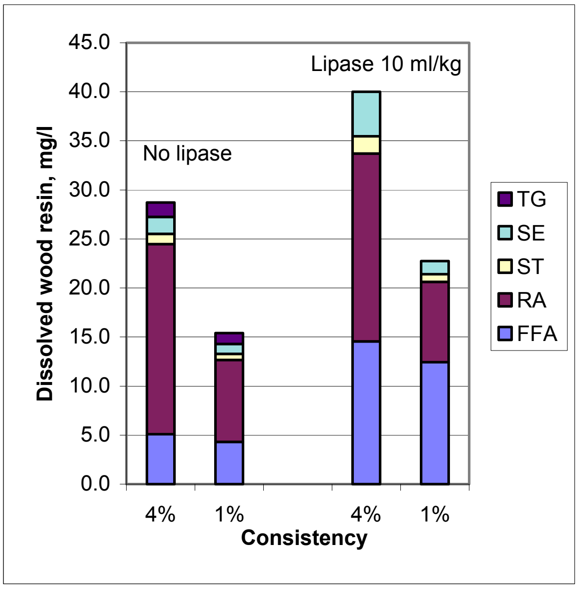


Figure 31. The effect of lipase treatment and the consistency of the pulp on the concentration of dissolved wood resin, TMP II.

Also at 1-% consistency, the usage of lipase increases the amount of “dissolved” steryl esters and sterols. This also supports the assumption that the usage of lipase may decrease the particle size of colloidal wood resin. Figure 32 shows that at pH levels of 3 and 5, the concentration of dissolved wood resin in the lipase-treated pulp is extremely low. This indicates that at lower pH levels, lipase does not increase the amount of “dissolved” wood resin and, hence, does not cause a reduction in the particle size of wood resin.

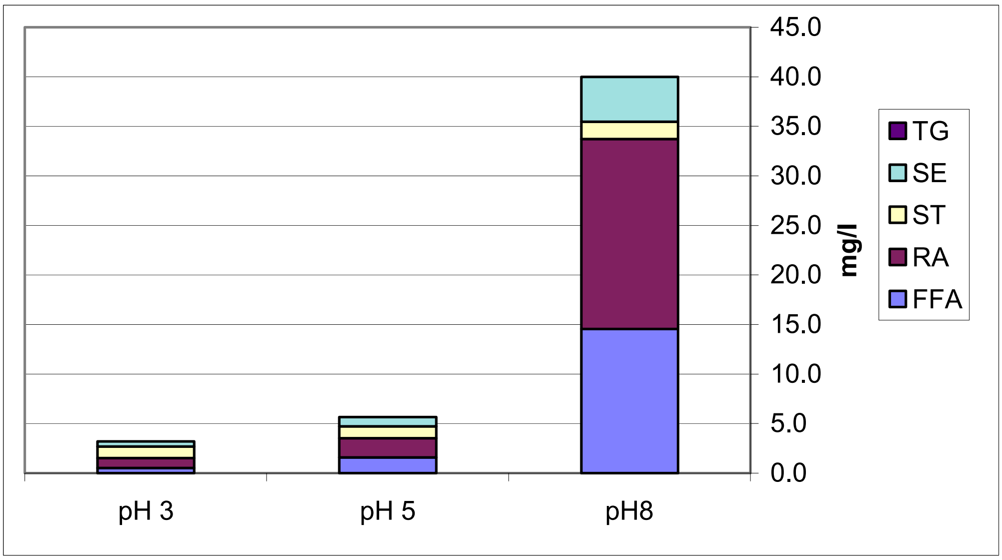


Figure 32. The effect of the pH level on the dissolution of wood resin with lipase-treated unbleached TMP II pulp. Lipase addition 10 ml/o.d.kg.

The results shown here indicate that the usage of lipase would not improve deresination efficiency in practice. The effect of lipase usage could be even slightly negative, one possible reason for which could be the formation of insoluble calcium soaps when the amount of free fatty acids is increased. These results also indicate that the natural changes in the ratio of wood triglycerides to free fatty acids, which is caused, for example, by the storage of the wood, does not have a significant effect on the efficiency of deresination.

The effect of lipase treatment on the behaviour of wood resin under different circumstances was studied more thoroughly in multivariate experiments that are presented later in chapters 5.1 and 5.2. These experiments also demonstrated that the usage of lipase did not promote the liberation of wood resin from pulp and, in some cases, even had a negative effect on wood resin liberation.

4.5 Peroxide Bleaching

Peroxide bleaching may have a significant effect on the wood resin content of the final pulp because part of the wood resin is degraded in bleaching that also tends to have an increasing effect on the liberation of wood resin to the pulp water phase. In this study, these two phenomena were more thoroughly evaluated.

Peroxide bleaching, when combined with washing, has shown to significantly decrease the resin content of pulp produced from pinewood [32, 43, 65, 67]. Quantitative results, that show the extent to which bleaching enhances the liberation of wood resin to the water phase as well as that to which wood resin is degraded in bleaching, were not reported in these studies.

In the case of Norwegian spruce this kind of quantitative information does exist [22, 55, 66]. This information as well as the results obtained from the mill measurements and laboratory studies are collected in Table VIII.

Table VIII also shows the proportion of wood resin that was liberated to the water phase from unbleached pulp. It can be seen here that the proportion of liberated wood resin observed in the different mill measurements is quite similar to that observed in the laboratory studies, which was about 50 %.

Table VIII. The proportion of wood resin liberated to the water phase from unbleached pulp, the effect of bleaching on the release of wood resin and the amount of wood resin degraded in the bleaching with Norwegian spruce TMP.

Mill measurements	Proportion liberated to the water phase, unbleached pulp, pH level 5, %	Proportion of fibre-bound wood resin liberated to the water phase after bleaching, pH level 7, %	Degraded in bleaching, %
[69]	60, 63		
[22]			15
[49]	56		
This study (1			
	56	**48**	**17**
	42	65	10 (assumed)
	48	50	12
Laboratory studies		pH level 5	
[66]		0	15 (assumed)
[21]	60		
[55]	46	80	18
[1](3	61		
This study			
TMP I (2	50-63	46	30
TMP II(2	55	30	13
Pilot-TMP(2	45	-42	18

1. Obtained from the mill measurements shown previously, see Chapter 3.2.
2. Obtained from the different experiments carried out on these pulp samples.
3. Obtained with pine CTMP.
4. This value was obtained in a similar way in both the laboratory studies and in the mill measurements by determining the proportion of fibre-bound wood resin in the unbleached pulp and calculating what proportion of this wood resin was liberated to the water phase in the bleached pulp.

4.5.1 The Chemical Changes in Wood Resin during Peroxide Bleaching

Ekman et al. [22] have studied chemical changes that occur in wood resin during peroxide bleaching very extensively. The major change that was observed was that the resin acids, which contained conjugated double bonds, were oxidised in bleaching, which led to a 50-% decrease in the resin acid content of the pulp. In other spruce wood resin components, there occurred only a slight alkaline hydrolysis of esterified fatty acids (6 %) and the oxidation of unsaturated fatty acids (6 %). Ekman et al. assumed that the oxidation products formed during bleaching are quite water soluble, which means that they are either extensively removed from the pulp in the subsequent washing or, if they remain in the pulp, do not cause similar deposition problems as does the native wood resin. In practice, this means that these oxidation products can be assumed to be destroyed.

The proportion of resin acids in spruce wood resin is about 20 %. In practice, this value is probably rather constant and should, therefore, be the amount of wood resin degraded in bleaching. Also, Table VIII shows that the proportions of wood resin observed to be degraded in bleaching in different studies were quite similar; about 15 %. The proportion of resin acids in pinewood is much higher. Thus, for pinewood, the proportion of wood resin degraded in bleaching is probably much higher than that for spruce wood.

The bleaching conditions may have an effect on the amount of wood resin degraded in bleaching. For example, only a small part of unsaturated fatty acids is oxidised in bleaching [22]. Under more severe bleaching conditions, the oxidative degradation of unsaturated fatty acids could be stronger. Figure 33 shows how the peroxide charge and bleaching consistency affect the amount of wood resin degraded in bleaching. The peroxide charge has an effect on the proportion of resin acids degraded, although the total amount of wood resin degraded in bleaching remains quite the same. Also, the bleaching consistency does not seem to significantly affect the amount of wood resin degraded in bleaching.

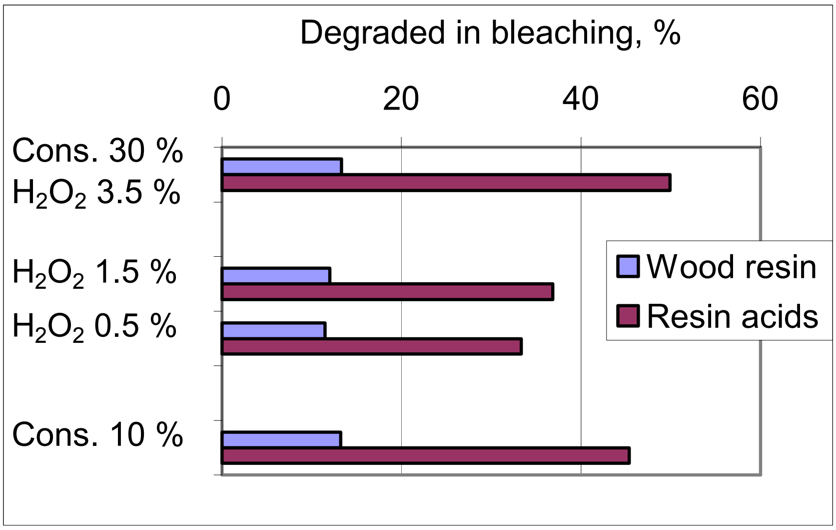


Figure 33. The effect of consistency and the peroxide charge on the proportion of wood resin degraded in bleaching, TMP II.

Ekman et al. showed that dissolved wood resin components are degraded most extensively in bleaching [22]. A high initial pH level promotes the dissolution of acidic wood resin components and, hence, the initial pH level in bleaching may have an effect on the degradation of wood resin. The effect of the initial pH level in bleaching can be seen in Figure 34. When the initial pH level increases, the amount of resin acids increases, which could be due to the slow mixing of the bleaching chemicals in these experiments. At higher initial pH levels, the peroxide can be consumed before it is thoroughly mixed to the thick pulp. The hydrolysis of triglycerides increases when the initial pH level is increased. This does not affect the total amount of wood resin because the same amount of free fatty acids is formed. This result indicates that the initial pH level does not affect the amount of wood resin degraded in the bleaching.

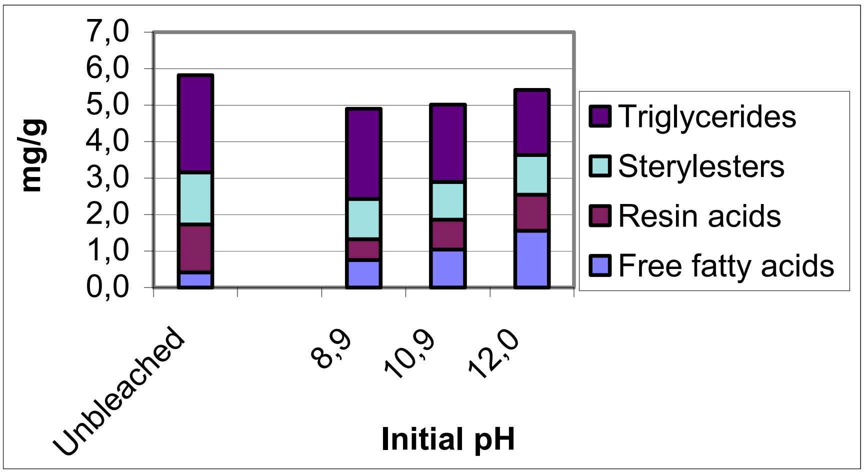


Figure 34. The effect of the initial pH in bleaching on the total amount of wood resin, TMP II.

According to these results, it would seem that the conditions in peroxide bleaching do not affect the amount of wood resin degraded in bleaching.

4.5.2 The Effect of Peroxide Bleaching on the Liberation of Wood Resin to the Pulp Water Phase

The results that show the extent to which bleaching affects the liberation of fibre-bound wood resin to the water phase can be seen in Table VIII, shown above. The deviation in the laboratory studies is very high, between -40 and 80 %, for which there is no clear reason. The negative effect of bleaching with Pilot-TMP could be related to the increase of the sodium concentration which, in this case, was 36 mM. In Figure 36 it can be seen that the negative effect of the addition of sodium on the liberation of wood resin to the pulp water phase is much more pronounced for Pilot-TMP pulp than for the other pulp samples.

The average effect observed in the laboratory studies seems to be slightly weaker than that observed in the mill measurements where the liberation of wood resin to the water phase is also promoted by the increased pH level. In the laboratory studies, on the other hand, the pH level in the bleached pulp samples was adjusted to the same level as in the unbleached samples.

According to the results presented in Table VIII, bleaching in itself, in a situation where the pH level is not increased after bleaching, causes the liberation of wood resin to the pulp water phase.

Figure 35 shows the effect of the initial pH level in bleaching on the proportion of different wood resin components in the pulp water phase. In the beginning, the proportion of neutral wood resin in the pulp water phase increases while that of acidic wood resin does not. One possible explanation for this could be that acidic wood resin is first dissolved from the wood resin colloids but then adsorbed to the fibre material, for instance, in the form of calcium soaps. At the points, where the initial pH level is above 11, the sodium concentration becomes so high - about 80 mmol/l - that this may cause the observed decrease in the proportion of wood resin in the pulp water phase.

Sundberg et al. [55] observed that adjusting the pulp pH level to 11.5 and then back to 5 significantly increased the amount of wood resin in the water phase. They assumed that wood resin, which is dissolved and dispersed under alkaline conditions, still remains in the water phase after the acidification of the pulp. In our experiment, this kind of behaviour was not probable because the bleaching consistency was much higher, 30 %, compared to that in their experiments, 10 %, and, hence, there hardly existed free water where the wood resin could be dissolved during bleaching. In addition, it could be assumed that with this mechanism, the increase should be best observed for acidic wood resin, although in this case the increasing effect was the clearest for neutral wood resin (triglycerides and steryl esters), see Figure 35.

There should, therefore, be some other explanation for the enhanced liberation of wood resin to the pulp water phase in bleaching. The demethylation of pectins increases linearly in the pH region between 8 and 12 [66]. This demethylation and the oxidation reaction caused by peroxide increase the charge of the fibre material [55]. Also, the oxidation reactions caused by peroxide are enhanced by the increased pH level. It could be then assumed that the increase in the initial pH level would also increase the charge of the fibre material, which would then increase the repulsion between the fibre material and the colloidal wood resin. This would subsequently lead to a higher proportion of wood resin in the pulp water phase. The next chapter, which discusses the effect of the additions of electrolytes on the behaviour of wood resin for bleached and unbleached pulp, supports this assumption to some extent.

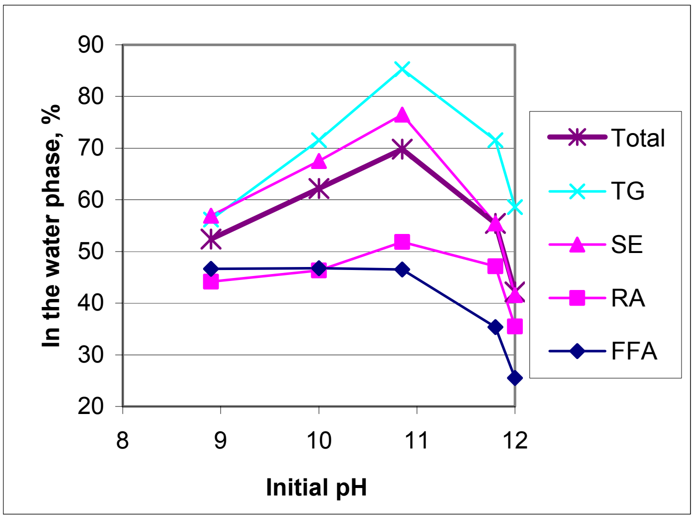


Figure 35. The proportion of wood resin in the pulp water phase vs. the initial pH level in bleaching. The levels of addition of sodium hydroxide were 1, 2, 3, 4, 4.5, and 6%. The dewatering was carried out at pH 5, TMP II.

4.6 Electrolytes (Na, Ca, Al)

The presence of electrolytes in the process may have a significant negative effect on the liberation of wood resin from pulp. The most interesting electrolytes as well as their sources in the process are sodium, which enters from peroxide bleaching, calcium, which enters with the paper machine with white water and which is also liberated from wood material and alum, which enters with the paper machine with white water. The aim of this study was to obtain information on how electrolytes affect the liberation of wood resin from pulp under different mill conditions.

Figure 36 shows the effect of the addition of sodium, calcium and alum on the residual turbidity in the case of different pulps and Figure 37 the effect of the addition of sodium and calcium on the residual wood resin content in the case of pilot-TMP.

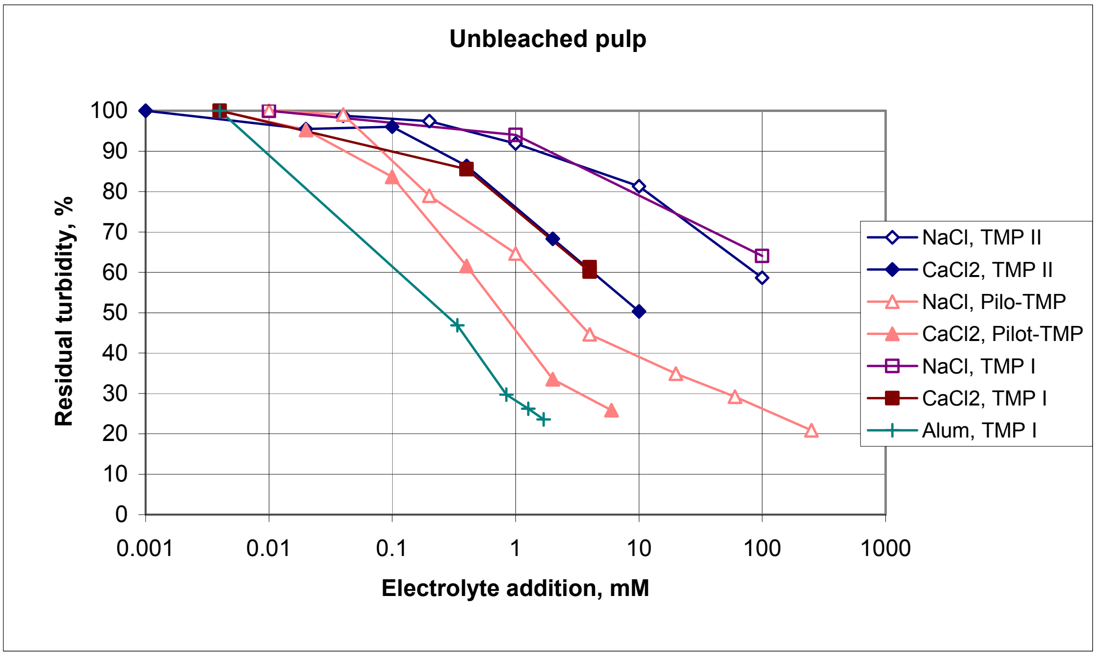


Figure 36. The effect of the addition of electrolytes on the residual turbidity of the pulp water phase with different pulp samples.

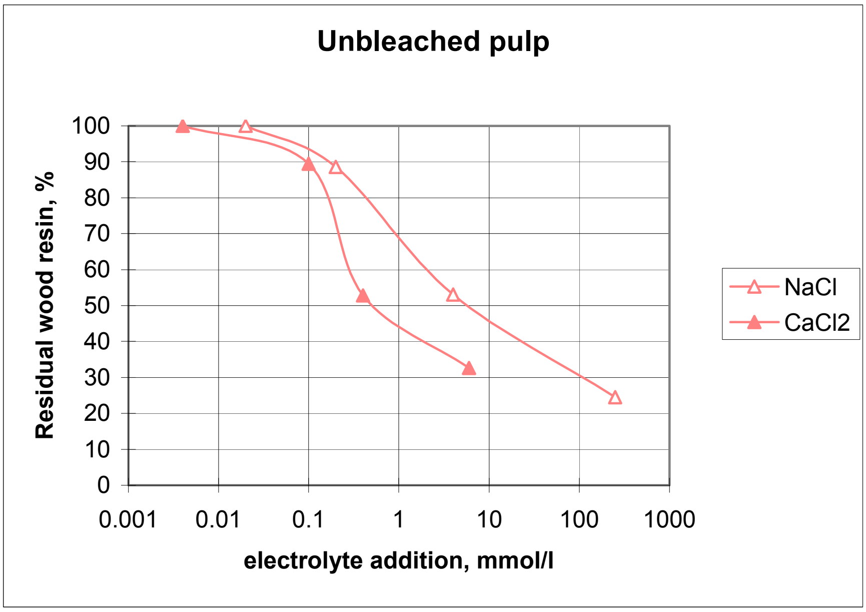


Figure 37. The effect of the electrolytes on the liberation of wood resin to the pulp water phase with Pilot-TMP. The wood resin analyses and the turbidity measurement shown in the previous chart show exactly the same results.

The concentrations of electrolytes in the existing processes can be in same magnitude as the effective concentrations shown in Figure 36 and Figure 37, especially if the pulp is bleached with peroxide or if the washing water, which comes from the paper machine, contains calcium or alum. For example, bleaching may increase the concentration of sodium in the process to 10 mM. It, therefore, seems that the presence of electrolytes may, in practice, have a significant effect on the liberation of wood resin from pulp.

Polymers dissolved from the wood during processing have an impact on the electrolyte-induced agglomeration of wood resin. Galactoglucomannans, released from the unbleached pulp, stabilise wood resin sterically [50, 58, 61, 66, 28]. In bleaching, these galactoglucomannans are deacetylated and mainly sorbed onto fibres, and hence no longer provide a sterical shield [66]. Pectin, which is also released in peroxide bleaching, may affect the behaviour of wood resin, especially in the presence of calcium [61].

In the existing process, the concentration of these dissolved substances is much higher than that observed in our experiments where pure water is used in dilution and the consistency is 4 %. Furthermore, in the existing process, calcium and alum are not mixed with the pulp together with pure water but, rather, with white water in which these substances are already dissolved. Both these factors may weaken the effects of the electrolytes on the behaviour of wood resin and were further studied by diluting the pulp with pure water or filtrate and adding the electrolyte either straight to the filtrate or after dilution to the pulp slurry, see Figure 38.

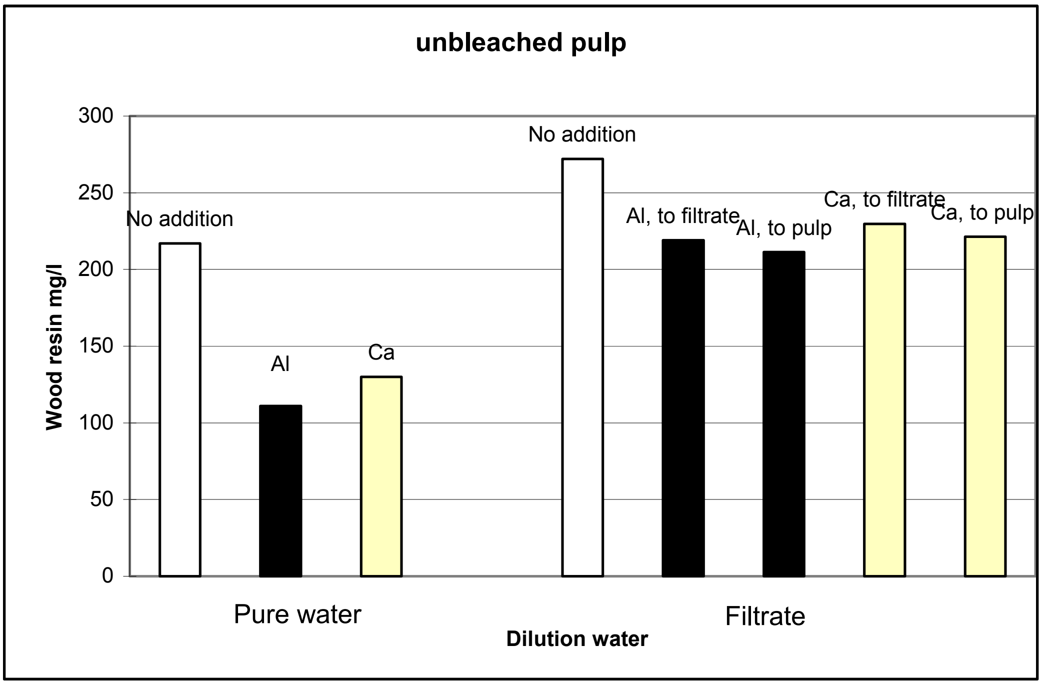


Figure 38. The effect of the alum and calcium on the liberation of wood resin from the pulp when the concentration of dissolved substances and order of addition was varied. The addition of alum was 0.34 mM and calcium 4 Mm. The filtrate used in the dilution was the same as that used when no additions were made except that the concentration of wood resin was reduced by filtering to 55 mg/l, TMP II.

The order of addition of the electrolytes did not have any significant effect on the amount of wood resin in the water phase, see Figure 38. When the addition was made directly to the pulp, the effect seemed to be slightly stronger than when the addition was made to the filtrate. In the latter case, a portion of the electrolytes is probably inactivated by adsorption to the dissolved organic material present in the filtrate.

When the pulp is diluted with the filtrate, the effect of the addition of the electrolyte on the amount of wood resin in the pulp water phase is clearly weaker than when the pulp is diluted with pure water, see Figure 38. Similar results were also obtained with the Pilot-TMP, see Figure 39.

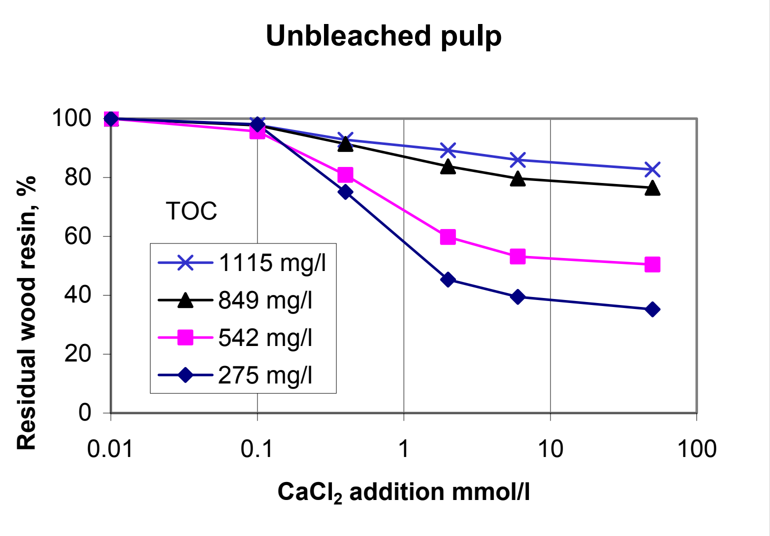


Figure 39. The effect of TOC concentrations on the calcium-induced agglomeration using the filtrate obtained from the unbleached pulp. Calcium was added to the filtrate and the turbidity was measured after centrifugation. Filtrates with different TOC concentrations were obtained by circulating the filtrate or by washing the same pulp sample twice, Pilot-TMP.

Figure 36 shows that, for Pilot-TMP pulp, the effect of the electrolytes on the amount of wood resin in the pulp water phase is much stronger than for the mill pulp samples (TMP I and TMP II). The reason for this could be the smaller amount of organic dissolved substances in the Pilot-TMP pulp than in the mill pulp samples. The TOC concentration in the Pilot-TMP pulp, 542 mg/l, was clearly lower than in the mill pulp samples, 800 mg/l and 1100 mg/l. The effects of calcium addition on the liberation of wood resin from mechanical pulp in two different studies [71, 70] were very similar as obtained with Pilot-TMP, see Figure 36 and also in these studies the amount of dissolved organic substances in the pulp was very small.

These results indicate that the effect of electrolytes on the liberation of wood resin from unbleached pulp depends heavily on the concentration of the dissolved substances in the process. This dependency is very probably attributable to changes in the concentrations of galactoglucomannans.

For bleached pulp, the concentrations of dissolved substances did not significantly affect the electrolyte-induced agglomeration of wood resin, see Figure 40. The slight differences observed here could be explained by the interaction of wood resin with calcium and pectins. At lower levels of calcium addition, filtrates with higher TOC concentration exhibit better stability because calcium is partly adsorbed to the pectins. At higher levels, pectins and calcium form a network that promotes the agglomeration of wood resin [60, 61] and, hence, there are clearly larger amounts of residual wood resin for filtrates with lower concentrations of TOC than for those with higher concentrations.

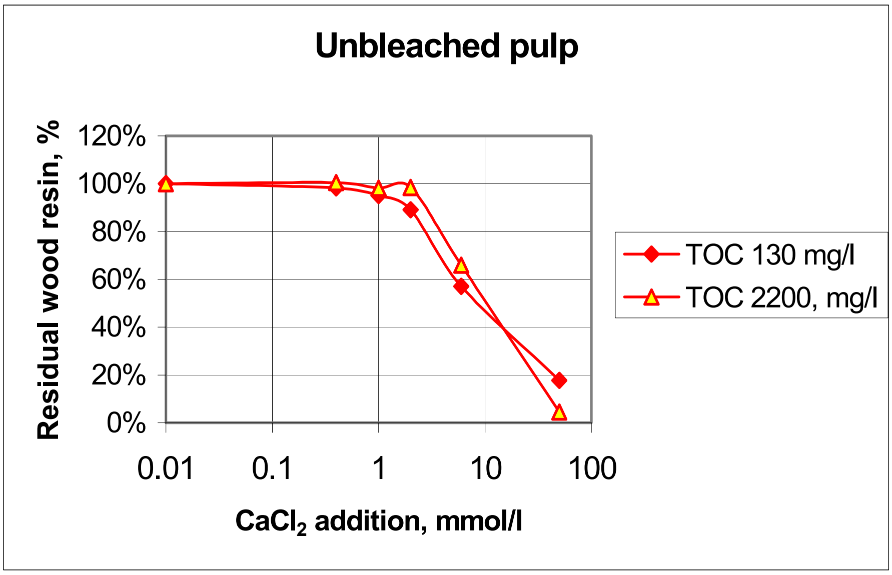


Figure 40. The effect of the concentration of TOC on calcium-induced agglomeration for a filtrate obtained from bleached pulp. The pulp was obtained from the bottom of the bleach tower during the mill measurement presented in Chapter 3.2. The experimental set-up was similar to that shown in Figure 39. The pH level of the filtrate was 7.

The effects of electrolytes on the agglomeration of wood resin in TMP-waters has been studied very extensively [62, 58, 61]. From the perspective of deresination, it is more essential to know what happens when the electrolyte is added to the pulp slurry. Possible differences between these two methods were studied by adding calcium directly to the pulp slurry as well as to the filtrate obtained from this same pulp. The difference between these two approaches was that in the former, the fibre material was present, while in the latter, the fibre material had been, for the most part, removed before the electrolyte was added. In contrast to the normal procedure used in this study, the electrolyte was added to the pulp slurry after mixing, which improves the comparability of the results since there were no differences other than the absence of the fibre material when the addition was made to the filtrate. After the addition of the electrolyte, the samples were gently mixed before centrifugation.

The experiments were carried out on unbleached (Figure 41) and bleached (Figure 43) pulp. The filtrate additions for TMP I pulp provided results that were very similar to those obtained in earlier studies [62, 58, 61].

When the electrolyte was added to the filtrate obtained from the unbleached pulp (Figure 41 and Figure 42), the negative effect was quite linear and could also be observed at very small levels of addition. In the experiment carried out with model dispersion, in which only wood resin existed [57, 50], the addition of less than 1mmol/l of calcium and less than

10mmol/l of sodium [50] did not cause any agglomeration. Also, Nylund has observed [39] that colloidal fibre material from unbleached pulp promotes the cationic-polyelectrolyte-induced agglomeration of the wood resin. These results lead to the assumption that unbleached fibre material promotes the electrolyte-induced destabilisation of wood resin, and, as a result, wood resin is probably attached to the fibre material.

The differences observed when adding the electrolyte to the pulp slurry support this assumption, see Figure 41 and Figure 42. At small levels of addition, the effect of calcium in the pulp slurry is weaker to that in the filtrate, while at higher levels, the effect of the addition of calcium on the pulp slurry is stronger. This difference could be explained by the fact that the adsorption of calcium to the fibre material decreases the repulsion between the fibre material and the colloidal wood resin. A small addition to the pulp slurry does not affect the repulsion since the amount of fibre material is large. At higher levels of calcium addition, the effect on the pulp slurry is stronger because there is now a larger fibre surface onto which the wood resin can be attached.

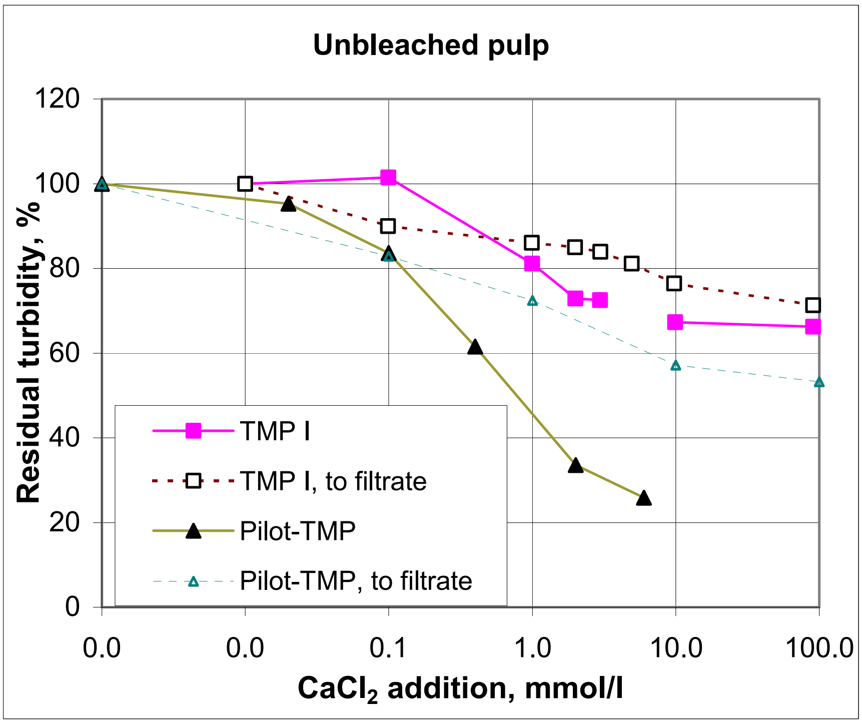


Figure 41. The effect of calcium on the amount of wood resin in the water phase. Calcium was added to both the unbleached pulp as well as to the filtrate obtained from the same pulp.

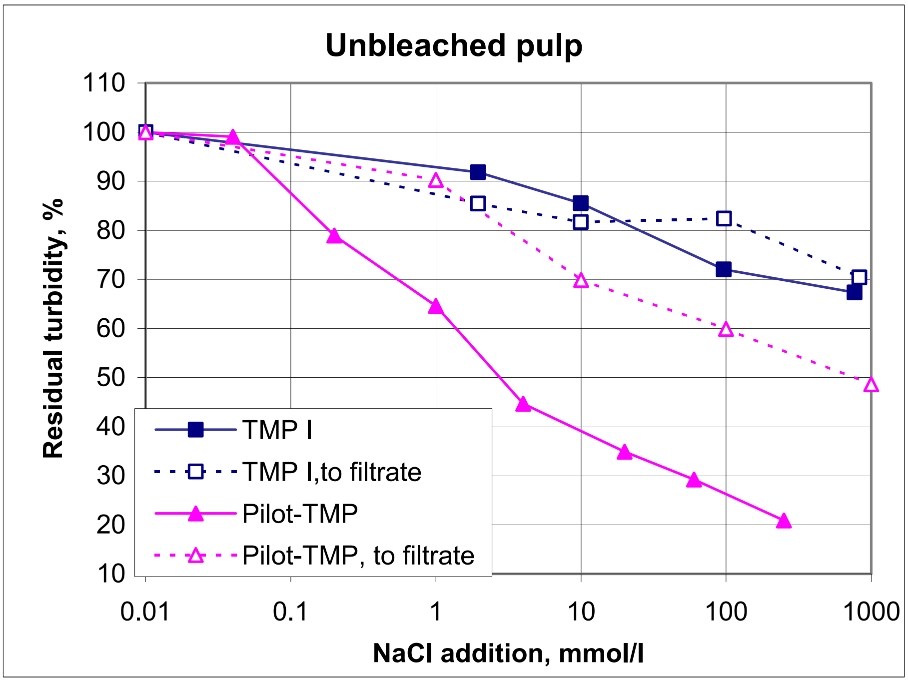


Figure 42. The effect of sodium on the amount of wood resin in the water phase. Sodium was added to both the unbleached pulp as well as to the filtrate obtained from the same pulp.

In the case of bleached pulp, the behaviour of wood resin is totally different, see Figure 43. The addition of calcium to the filtrate had a stronger effect on the wood resin than in situations where calcium is added to the pulp slurry.

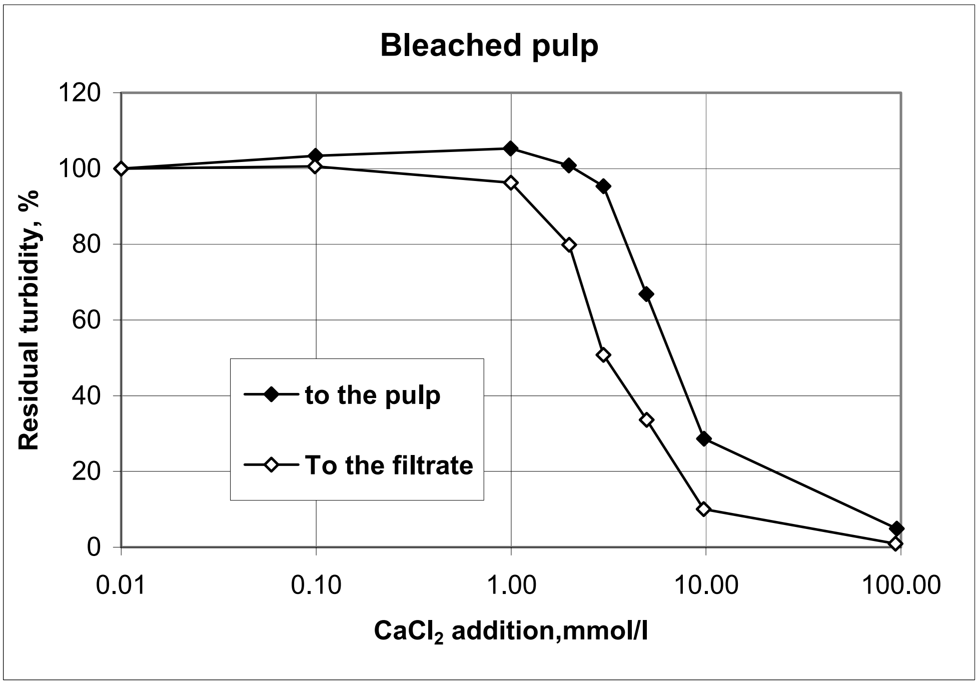


Figure 43. The effect of calcium on the amount of wood resin in the water phase. Calcium was added to both the bleached pulp as well as to the filtrate obtained from the same pulp, TMP I.

This results indicate that the fibre material in the bleached pulp does not promote the destabilisation of wood resin, which supports the earlier assumption, presented at the end of the previous chapter, that bleaching increases the repulsion between the fibre material and colloidal wood resin. This also indicates that destabilisation in the bleached pulp may lead to the agglomeration of wood resin.

In the case of the pulp slurry, the weaker effect of the addition of calcium could be a result of the adsorption of calcium to the fibre material, see Figure 44, which would then decrease the amount of calcium in the surrounding liquor.

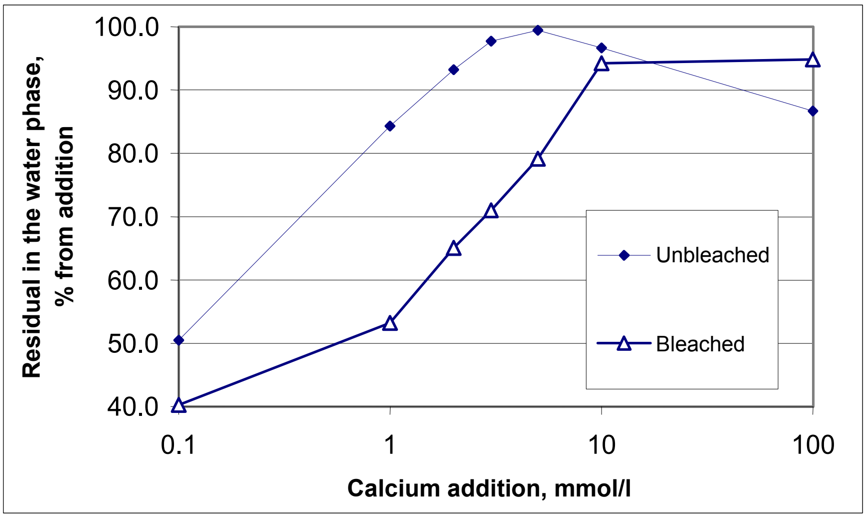


Figure 44. The proportion of calcium in the pulp water phase when calcium was added to the pulp slurry, TMP I.

4.7 The Use of Dispersing Agents

Dispersing agents have been traditionally used in mechanical pulping mainly to prevent the precipitation of wood resin in grinding or to the refining blades [3]. Dispersing agents are usually added in small amounts, well below 0.1 % of the pulp. It has been proposed that the removal of wood resin from mechanical pulp could be enhanced by the use of dispersing agents [1], but so far, no results related to the effect of dispersing agents on the efficiency of deresination have been published.

In Figure 45, it can be seen that fatty alcohol ethoxylates have a clear but not very strong increasing effect on the amount of wood resin in the pulp water phase. In the case of unbleached pulp, the concentration of wood resin increased by about 20 mg/l, and in that of bleached pulp, by about 10 mg/l. The increase in the concentration of wood resin does not result from the liberation of colloidal wood resin from the pulp but, rather, from the dissolution of wood resin. The addition of a dispersing agent increased the amount of dissolved wood resin by an amount very similar to that by which the wood resin in the water phase was increased, see Figure 46. The observed dissolution of wood resin was very probably caused by the micellar solubilisation of the wood resin. The CMC value for the fatty alcohol ethoxylate is very low, about 5 mg/l [47], and the concentration in the pulp slurry at the highest addition point 160 mg/l, which makes the formation of micelles and the micellar dissolution of wood resin very probable.

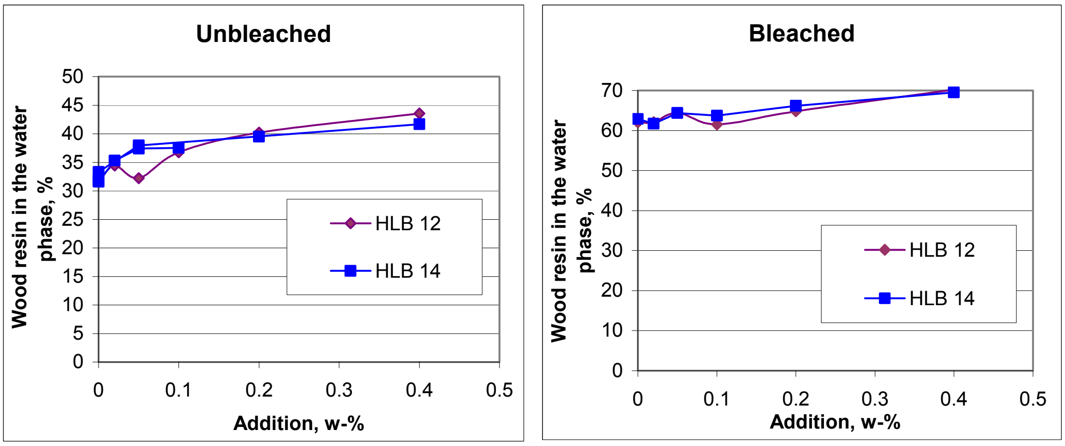


Figure 45. The proportion of wood resin in the pulp water phase versus the addition of fatty alcohol ethoxylates with different HLB values. The unbleached pulp was pilot-TMP and the bleached pulp was obtained from the discharge of a wash press.

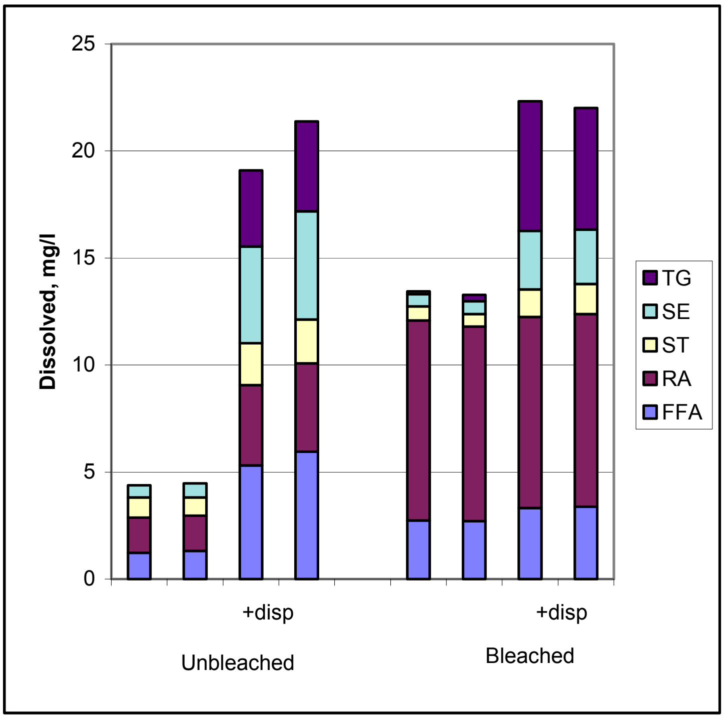


Figure 46. The effect of fatty alcohol ethoxylate HLB 12 0.4 w-% on the dissolution of wood resin. Analyses were carried out at the experimental points shown in Figure 45.

The dissolution of wood resin can be also seen in the fall of the ratio of turbidity to wood resin, measured from the pulp water phase, see Figure 47, and even more so as a fall in turbidity, when the dispersing agent was added to the filtrate, see Figure 48 and Figure 49. The stronger influence in the case of the addition of the dispersing agent to the filtrate indicates that fibre material inactivates the interaction between the dispersing agent and wood resin. Possible explanations for this could be the adsorption of the dispersing agent on the fibre material. The dissolving effect of the dispersing agent seems to be quite similar for different wood resin groups, see Figure 50.

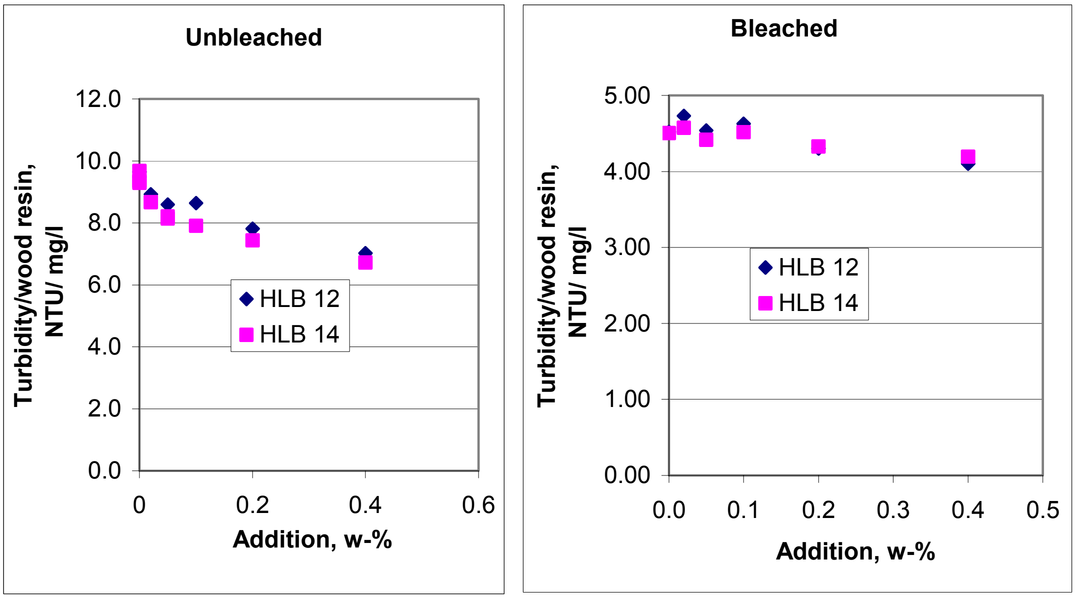


Figure 47. The ratio of turbidity to wood resin versus the addition of fatty alcohol ethoxylate. The results were obtained from the experiment shown in Figure 45.

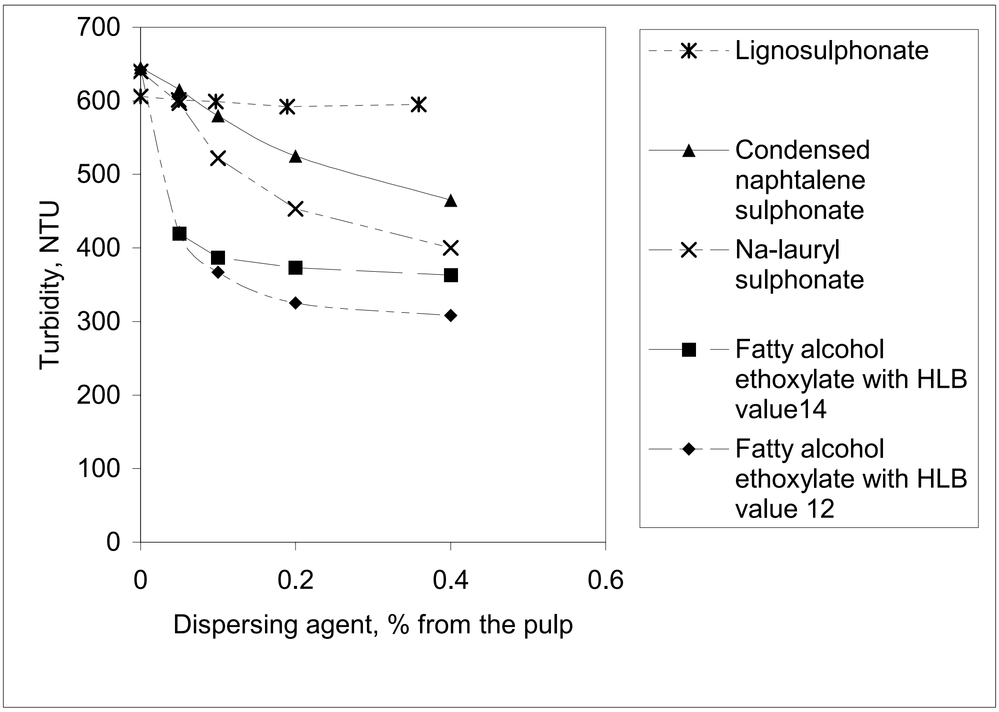


Figure 48. The effect of different dispersing agents on turbidity when added to the filtrate obtained from the unbleached pulp, Pilot-TMP.

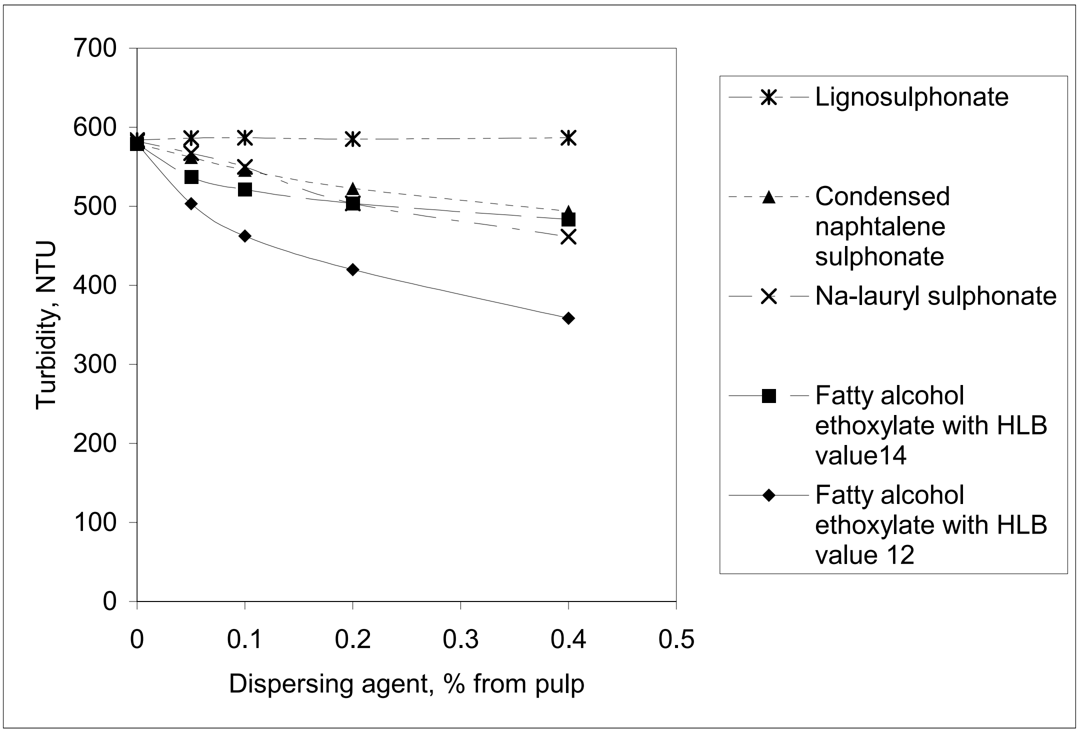


Figure 49. The effect of different dispersing agents on turbidity when added to the filtrate obtained from the bleached pulp. The bleached pulp was obtained from the discharge of a wash press.

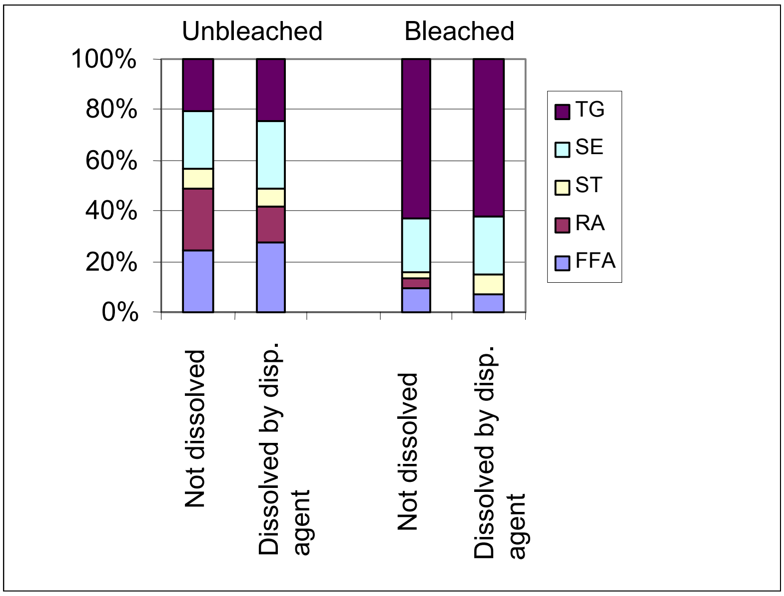


Figure 50. The effect of fatty alcohol ethoxylate HLB 12 0.4 w-% on the dissolution of different wood resin groups. The analyses were carried out on the experiment shown in Figure 45

In the system where the liberation of wood resin was restricted by the presence of calcium, see Figure 51, the effect of the dispersing agent on the proportion of wood resin in the water phase was quite significant.

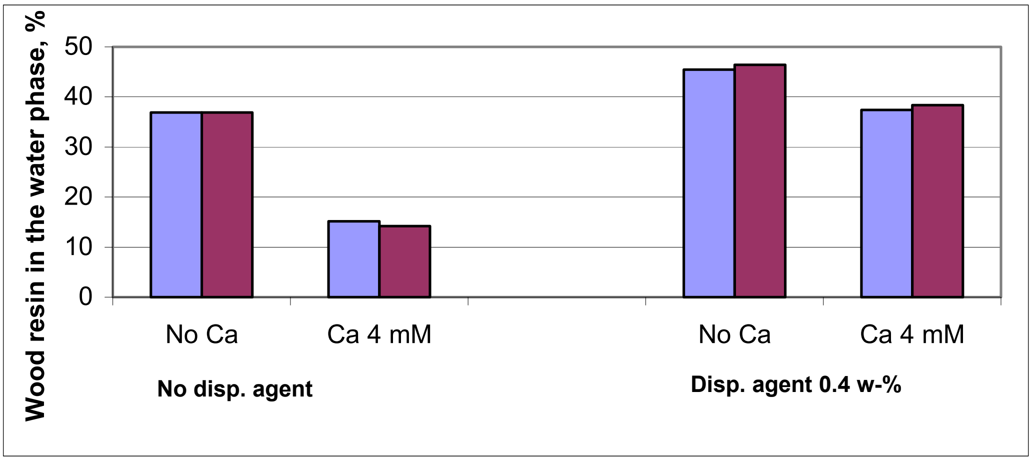


Figure 51. The effect of the addition of fatty alcohol ethoxylate and $CaCl_2$ on the proportion of wood resin in the pulp water phase. The dispersing agent was added before calcium was, Pilot-TMP.

In the experiments involving other dispersing agents, the amount of wood resin was not analysed, although the turbidity measurements do indicate that the effect of the dispersing agents on the liberation of wood resin from the pulp was not significant, see Figure 52.

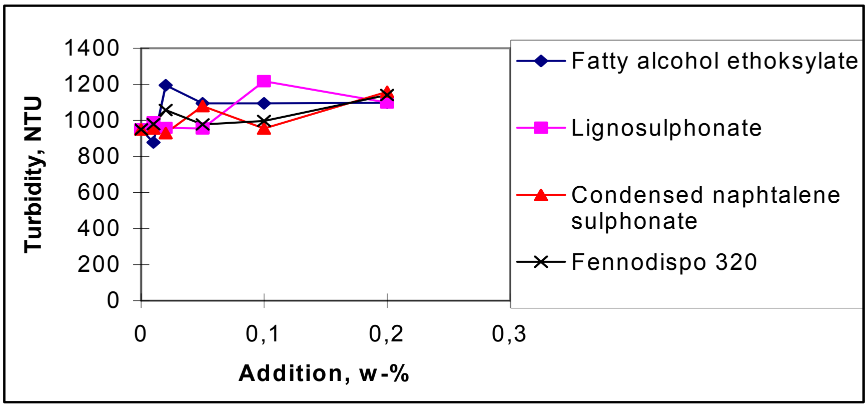


Figure 52. The effect of different dispersing agents on the turbidity measured from pulp water phase, TMP I.

This short evaluation indicates that the low amounts of dispersing agent, usually added in the course of refining, do not influence the liberation of wood resin from pulp. Also, the usage of dispersing agents in larger amounts does not automatically improve the liberation of wood resin from pulp, although under certain conditions, the use of a dispersing agent may have a increasing effect.

4.8 The Degree of Refining

4.8.1 The Proportion of Wood Resin in the Pulp Water Phase

In principle, the degree of refining may affect the proportion of wood resin in the water phase in two possible ways. Firstly, pulp with a lower freeness value has received more intensive treatment during refining, which may enhance the release of wood resin from the parenchyma cells. Secondly, the adsorption of wood resin onto the pulp may depend on the specific surface area of the pulp. In pulp with a low freeness value, the specific surface area is higher and, thus, the amount of wood resin adsorbed onto the pulp can also be larger.

Wood resin is located in the wood tissue mainly in resin channels or inside parenchyma cells. Canal resin can be already removed from the chips by pressing and during refining the resin channels brake up completely. Parenchyma resin cannot be removed from the chips by pressing [15]. According to studies related to the breaking of parenchyma cells during refining of TMP [15, 35], it is possible that the liberation of wood resin from the parenchyma cells already takes place almost completely in pulp which has been defibrated to a higher freeness value.

The wood resin in the parenchyma cells is comprised mainly of triglycerides and steryl esters, while that located in the resin channels is composed mainly of resin acids [12]. In the study carried out on TMP, which was refined to a freeness value of 120 ml, the composition of the wood resin in the pulp water phase was the same as that of the resin in the pulp [21]. This result indicates that both the parenchyma and channel resin were equally accessible for release to the water phase and, hence, there should not exist any wood resin captured inside unbroken parenchyma cells.

If the liberation of wood resin from the parenchyma cells is influenced by the freeness value of the pulp, a decrease in the level of freeness of the pulp should cause the proportion of triglycerides and steryl esters to increase and that of resin acids to decrease in the pulp water phase. Figure 53 and Figure 54 show that the proportions of different wood resin groups remain quite constant when the freeness value of the pulp is increased from 100 to 500 ml CSF. For the steryl esters and triglycerides, only a very slight increase can be observed. These results confirm that the degree of refining does not have significant effect on the accessibility of wood resin for liberation from the parenchyma cells. These results also indicate that the parenchyma cells in pulp, that has a high freeness value, are already damaged in such of way that all the wood resin located in these cells is accessible for liberation to the pulp water phase.

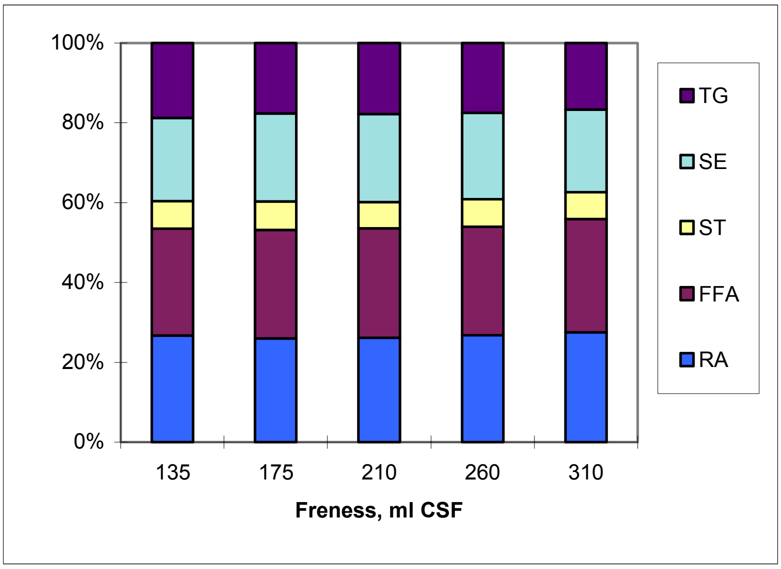


Figure 53. The effect of freeness on the proportions of different wood resin groups in the water phase. The freeness values used in here were measured from the pulp samples before dewatering. The freeness values measured after hot disintegration were slightly lower, namely, between 100 and 250 ml CSF, Pilot-TMP.

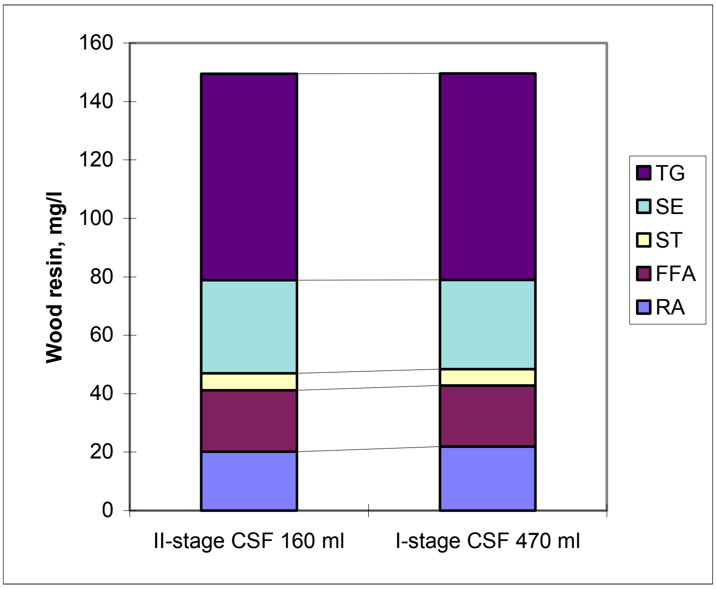


Figure 54. The effect of the freeness value on the amount of different wood resin components in the pulp water phase. Pulp samples were taken from the same pulp production line after I-stage and II-stage refiner. The freeness values were measured from the pulp after hot disintegration, TMP II.

It has been observed that the wood resin content of fines is higher than that of fibres and it was also assumed that this difference is caused by the larger surface area of fines in comparison to that of fibres [30]. When the degree of refining is increased, the proportion of fines and, hence, the surface area of the pulp increases. This could have a increasing effect on the adsorption of wood resin onto the pulp. In Figure 54 and Figure 55, it can be seen that the amount of wood resin in the pulp water phase is independent of the freeness value. Therefore, these results also indicate that the degree of refining does not have a significant influence on the amount of wood resin adsorbed onto the pulp.

According to these results it seems that the degree of refining does not influence the liberation of wood resin from the pulp.

4.8.2 The Effect of the Freeness Value on the Retention of Water-released Wood Resin in Dewatering

When the freeness value of the pulp decreases, the retention of wood resin has to increase, and the main question is how much the freeness value can affect retention in this case?

From Figure 54, it can be seen that when the freeness value of the pulp falls from 310 to 135 ml, the retention of wood resin is almost doubled.

For lower freeness values, the increase in retention is much sharper, Figure 56. Similar results were also obtained earlier in the measurements carried out in the mill-scale dewatering devices, Figure 12. Figure 56 also shows that the retention of substances, which cause turbidity, is higher compared to the retention of wood resin. This similar phenomenon was also observed and discussed in the mill measurements, shown earlier in the Chapter 3.2.3.

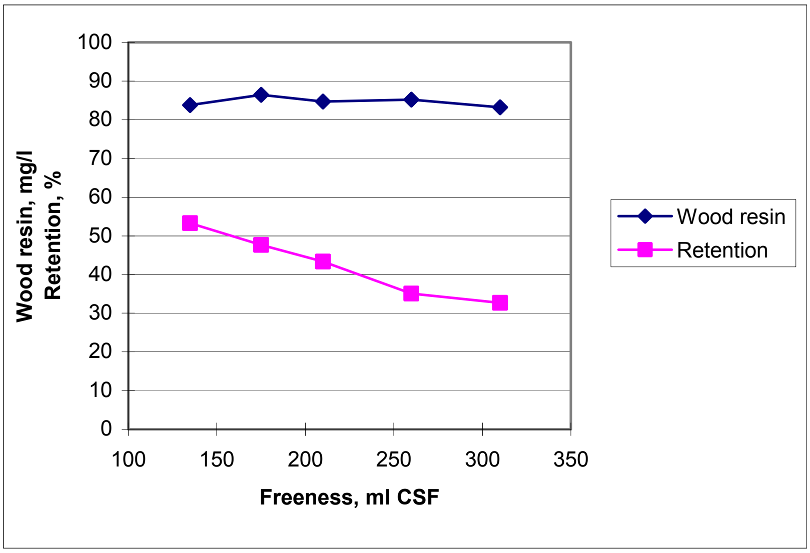


Figure 55. The effect of freeness on both the amount of water-released wood resin in the pulp and retention during dewatering, Pilot-TMP. The determination of retention is described in the Chapter 2.3.

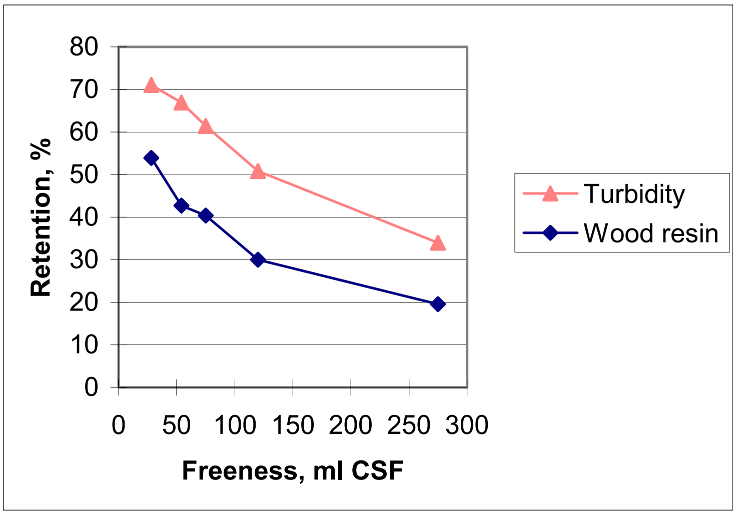


Figure 56. The retention of wood resin and turbidity-causing substances for pulp samples refined to different levels of freeness with Valley-beater, Pilot-TMP.

4.9 The Quality of the Dilution Water

One important question in the evaluation of the efficiency of deresination is how the liberation of wood resin from the pulp alters if the consumption of water or the water connections and, hence, the quality of the dilution water in the process is changed. Laboratory experiments have shown that the circulation of the filtrate substantially decreases the liberation of wood resin from pulp [1, 21]. The aim of this study was to find out how strongly alterations in the quality of the dilution water affect the liberation of wood resin from the pulp and what the possible reasons for this effect are.

The effect of the quality of the dilution water on the liberation of wood resin was studied by diluting bleached and unbleached pulp with different types of filtrates obtained from a process. These experiments were carried out in the same pulping plant as were the mill measurements that are discussed in chapter 3.2. The unbleached pulp used in the experiments was obtained from the second stage refiner and the bleached pulp from the discharge of the HC-peroxide bleaching tower, see Figure 7. The names and descriptions of the dilution water samples used in the experiments are listed in Table IX.

Table IX. The names and descriptions of the dilution water samples used in the experiments. The number after the name refers to the concentration of wood resin in the dilution water in mg/l. The information characterising the properties of these dilution water samples is shown in Appendix 12.

Name	**Description**
NF and UF	Permeate of nano- or ultrafiltrated wash press filtrate
Bleached 160	Filtrate from wash press
Unbleached 50	Superclear filtrate from disk filter
Unbleached 200	Filtrate from the bleach press
PM WW	Paper machine circulation water
Unbleached 300	Obtained by washing the unbleached pulp with the filtrate from the bleach press.
Bleached 320	Obtained by washing the bleached pulp with the filtrate from the wash press.
Pure	Ion-exchanged water

For both pulp samples, the difference between the highest and lowest result, when different dilution water samples were used, was only about 15 %, see Figure 57. The variation in the pH level explains about half of the observed variation and, thus, the effect of the properties other than the buffer capacity of the dilution water is quite small. This result implies that even if the consumption of water or the water connections in the process are altered considerably, it is possible that the behaviour of the wood resin will not change much.

Detailed information on how the different properties of the dilution water affect the liberation of wood resin to the pulp water phase can also be obtained from Figure 57:

- The only difference between the dilution water samples, which are referred to as unbleached 50 and 200, is that the concentration of wood resin is higher in the latter. Also, the amount of wood resin liberated to the water phase is smaller both in the case of the bleached and unbleached pulp when “unbleached 200” is used as the dilution water in comparison to “unbleached 50”. This result implies that the concentration of wood resin in the dilution water has an effect on the liberation of wood resin from the pulp.
- The concentration of electrolytes in the membrane filter permeates and in the paper machine white water was so high, see Appendix 12, that this could explain why the results obtained with these filtrates are lower compared to those obtained with ion-exchanged water. For permeates, the result is also clearly lower than for the filtrate (bleached 160) from which these permeates were made. This could be explained by the fact that membrane filtration removes a major part of wood polysaccharides, such as galactoglucomannans and pectins, while significant amounts of electrolytes (sodium and calcium) remain in the permeate, see Appendix 12. Glucomannans stabilise the wood resin against electrolyte-induced destabilisation, while pectins may bind calcium [66,60].
- The quality of the dilution water considerably affects the ambient pH level, which, in turn, also affects the liberation of wood resin to the pulp water phase.

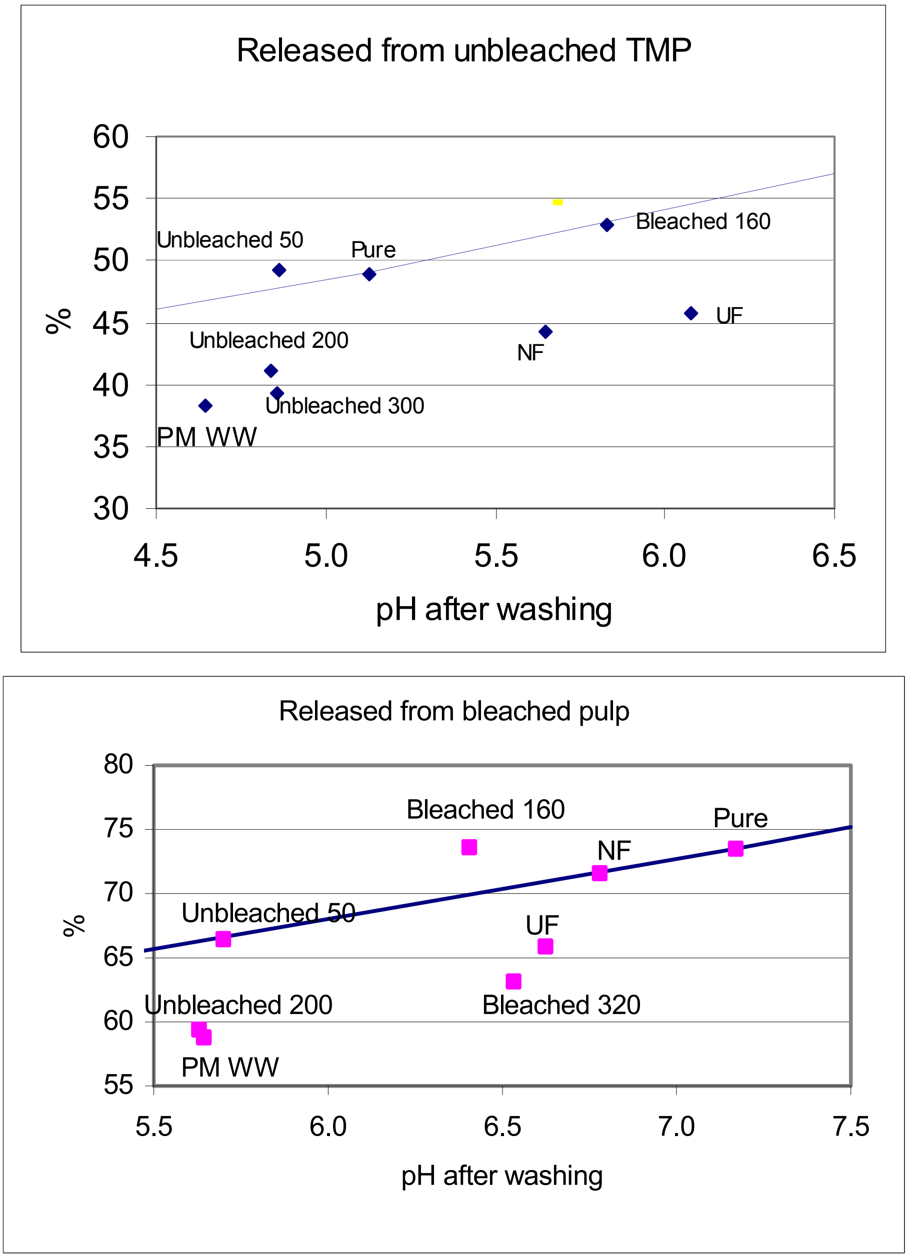


Figure 57. The liberation of wood resin from the pulp when different dilution water samples were used. The explanations for the labels are given in Table IX. The line drawn through the pure water point shows the assumed effect of the pH level. By comparing the other points to that line the effect of the pH level can be eliminated. The results are based on between 1 and 5 parallel experiments, and the results of the individual experiments can be seen in Appendix 11.

5. INFORMATION OBTAINED WHEN SEVERAL WASHING VARIABLES WERE VARIED SIMULTANEOUSLY

Two multivariate experiments were conducted in order to ascertain the effect and cross-effect of different factors on the liberation of wood resin from the pulp and also on the retention of water-released wood resin in dewatering. Also, more information on the effects of individual washing variables and the basic phenomena related to the behaviour of wood resin was obtained.

5.1 Multivariate Experiment I: Bleaching, Mixing Time, Calcium Addition, pH Level and Lipase Treatment

The main aim of the first multivariate experiment was to obtain information on the cross-effects of different factors as well as on the effects of lipase treatment and bleaching on the liberation of wood resin from the pulp. Also, information on the effects of mixing, the pH level and calcium addition as well as on the effects of all these factors on the retention of water-released wood resin in the dewatering was obtained.

The main structure for the experiments was a two-level four-factorial experiment which consisted of 16 experimental plus two centre points. For the unbleached pulp, this experimental layout was prepared twice. Also, one additional series was constructed, for which six experimental points were replicated. For the bleached pulp, two different series were constructed, one normal and one shorter series, for which experimental points with short mixing times were replicated. Thereby, the total amount of experimental points was 68. The mixing time and level of addition of calcium varied slightly amongst the different series. Also, the pH level was not adjusted exactly at the target value. Table X shows the factors analysed and the most used values. The accurate values of the variables at different experimental points are shown in Appendix 7. Scaled values were used for the variables in the calculation of the regression coefficients. The original values were linearly scaled in accordance with Table X.

The wood resin analyses carried out on the pulp water phase at each experimental point are shown in Appendix 7. The pulp samples used in the experiment consisted of unbleached, bleached and lipase-treated bleached TMP I pulp. The wood resin analyses carried out on these pulp samples are shown in Appendix 8.

Table X. The factors in the first multivariate experiment, the most used values and the scaling of these values for the regression analysis.

Factor	Level 0	Level 1
1. Bleaching	Unbleached	H_2O_2-bleached
2. Mixing time	5 min	90 min
3. Calcium addition	0 mM	2 mM
4. pH level	5	8
5. Lipase treatment	no	yes

5.1.1 The Proportion of Wood Resin in the Pulp Water Phase

The proportion of wood resin liberated to the pulp water phase at each experimental point was calculated on the basis of the analyses carried out on the pulp samples (Appendix 8) and on the pulp water phase (Appendix 7). The thus calculated values are shown in Appendix 6, while the results from the multivariate regression analyse are shown in Table XI.

Table XI. The effects and cross-effects of different factors on the proportion of wood resin in the pulp water phase.

$R^2 = 0.90$	Effect, %-units	P-value	95 % Interval of confidence, +/- %-units
Constant	**55.3**	1.4E-42	2.9
Bleaching	**11.8**	3.7E-07	4.1
Mixing time	**5.5**	0.00024	2.8
Calcium	**-13.5**	5.9E-10	3.6
pH level	**13.3**	2.9E-17	2.2
Lipase	**3.6**	0.00759	2.6
Bleaching-mixing	6.4	0.00625	4.5
Bleaching-calcium	**7.1**	0.00496	4.9
Bleaching-lipase	**-8.7**	0.00010	4.2
Calcium-pH level-lipase	**-8.4**	0.00110	4.9

The constant in Table XI (55.3 %) shows the proportion of wood resin in the pulp water phase when all variables are assigned the value 0. This is the situation when the pulp is unbleached, the mixing time of the pulp slurry is 5 min, calcium is not added, the pH level is 5 and lipase is not used (Table X). The result of 55.3 % is quite the same as that obtained earlier with TMP I and TMP II under similar conditions. The effects of 5.5, -13.5 and 13.3 % for the mixing time, calcium addition and pH level, respectively, are quite similar to those observed earlier in this study. In addition, the effect of bleaching was clearly positive, 11.8 %, as expected.

Lipase treatment had a slight positive effect (3.6 %), but positive lipase-pH level interaction was not obtained. This agrees very well with the result shown in Figure 58, according to which lipase treatment, combined with elevated pH levels, did not increase the amount of dissolved wood resin.

At elevated pH levels, when calcium was present, (calcium-pH level-lipase, -8.4 %), lipase treatment had a negative effect on the proportion of wood resin in the pulp water phase. It can also be seen in Figure 58 that calcium addition reduced the amount of dissolved fatty acids. This could be a result of the formation of insoluble calcium soaps.

For bleached pulp, lipase treatment had a negative effect on the proportion of wood resin in the pulp water phase (bleaching-lipase, -8.7). In the mill (Chapter 3.2) and laboratory study (Chapter 4.5.2) it was also observed that during bleaching, neutral wood resin was liberated to a greater extent to the pulp water phase than was the acidic wood resin. This could also be a result of the formation of insoluble calcium soaps.

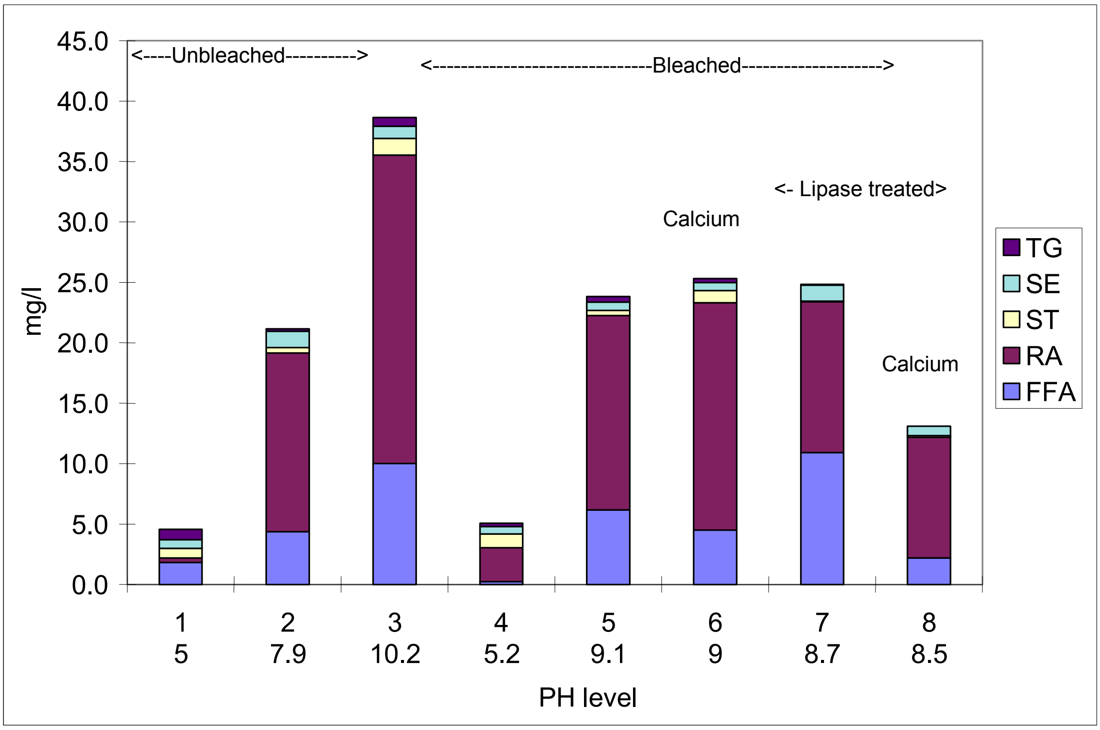


Figure 58. The concentration of dissolved wood resin under different conditions. The level of the addition of calcium was 1 mmol/l. The unbleached pulp was TMP II and the bleached pulp TMP I.

The positive bleaching-calcium interaction (7.1 %) shows that, for bleached pulp, the negative effect of the addition of calcium is not as strong as it is for unbleached pulp. This result is exactly the same as that obtained in chapter 4.6, see Figure 41 and Figure 43.

5.1.2 Differences in the Liberation of Various Wood Resin Groups to the Pulp Water Phase

It has been assumed that, during the intensive defibering of mechanical pulp, the different wood resin components are completely mixed and the colloids formed are, therefore, chemically homogenous. [10]. This means that the liberation of different wood resin components to the pulp water phase should be very similar except at higher pH levels where acidic wood resin components, especially resin acids, are dissolved.

This multivariate experiment also provided information on the liberation of different wood resin groups to the pulp water phase. These results were analysed by comparing how the proportion of certain wood resin group in the pulp water phase altered in relation to that of the other wood resin groups in the pulp water phase. This rather complex method was used because it directly shows the difference between the behaviour of different wood resin groups. Regression analyses could also have been carried out on a proportion of a single wood resin group in the pulp water phase, although in such a case, the result would have been a set of rather similar regression models, which would have made the actual differences between the various wood resin groups difficult to observe.

The ratio of the following wood resin groups was calculated:

- Resin acids to wood resin

- Free fatty acids to the ratio of wood resin except resin acids
- Steryl esters to the ratio of wood resin except resin acids

When the behaviour of free fatty acids and the steryl esters was evaluated, the resin acids were not included in the wood resin because, in this way, the variation caused by the resin acids could be eliminated. The numerical values are shown in Appendix 6.

Resin Acids

Figure 59 provides an approximate view of the results. In the mixing time, addition of calcium and pH level, there are differences which are not shown in the Figure, see Appendix 6. Furthermore, eight experimental points, in which the variables had a centre value, are not included in Figure 58. The results from the multivariate regression analysis are shown in Table XII. In the first series, that was obtained for bleached pulp, points 9 to 12 were removed because in the gas chromatogram, among the resin acids, there was an abnormal peak, that increased the measured concentration of the resin acids.

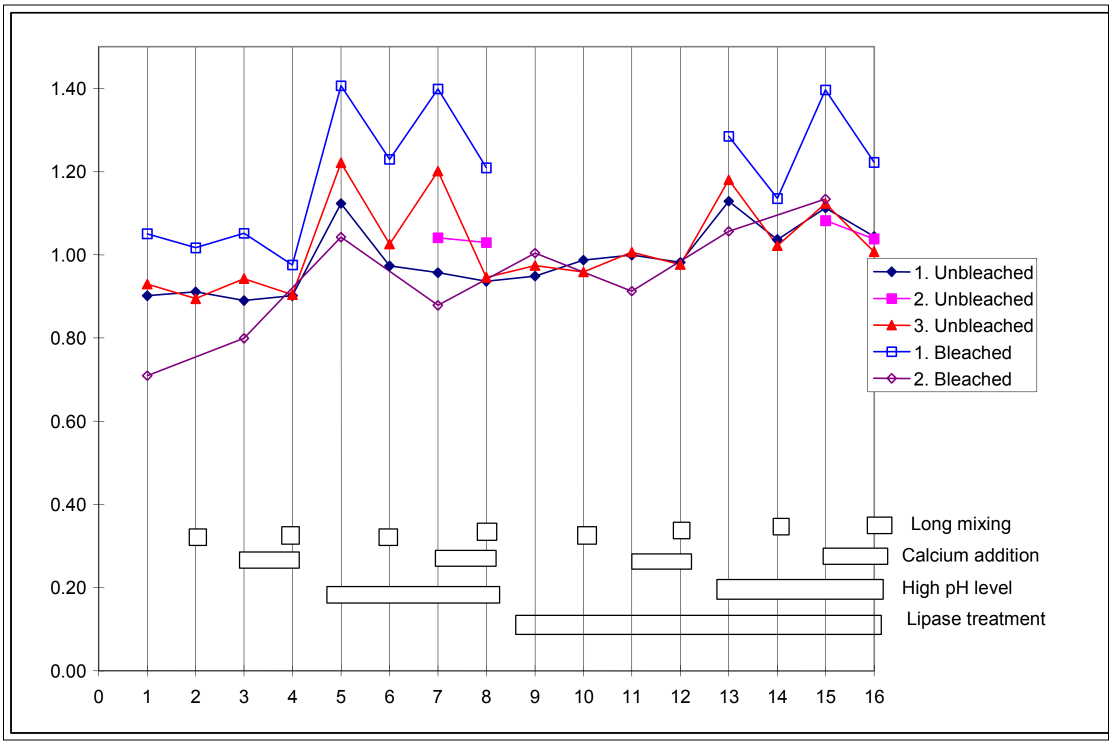


Figure 59. The liberation of resin acids in relation to the liberation of all wood resin components to the pulp water phase. The diagram shows the results that were obtained at separate experimental points.

Table XII. The liberation of resin acids in relation to the liberation of all wood resin components to the pulp water phase. The table shows the regression coefficients and P values.

$R^2 = 0.56$	Regression coefficient	P value
Constant	0.92	
pH level	0.29	0.003
$(\text{pH level})^2$	-0.12	0.195
pH level-mixing	-0.10	0.017
pH level-bleaching	0.07	0.156
Lipase	0.05	0.045
Bleaching-mixing	0.11	0.054

The R^2 value as well as the P values for the regression model are very small, see Table XII. This is principally because the results obtained, for bleached pulp, in the first series are much higher compared to those obtained in the second series.

The coefficient in the regression model is 0.92 and is, therefore, unequal to one, which means, that at a pH level of 5, resin acids are not released to the pulp water phase to same extent as are the other wood resin components. A study carried out by Ekman et al. [21], in which the proportion of resin acids liberated to the pulp water phase at a pH level of 5 was also slightly smaller than that of the other wood resin components, provides some support for these results.

According to Table XII, an increase in the pH level promotes the liberation of resin acids more than that of the other wood resin components, which was to be expected and is caused by the dissolution of resin acids at elevated pH levels, where an increase in the mixing time reduces the ratio of resin acids to wood resin components. The explanation for this is that the dissolution of resin acids at elevated pH levels takes place more quickly than does the dispersion of wood resin from the pulp and, thereby, during a longer mixing time, the amount of colloidal wood resin in the pulp water phase increases, while the relative proportion of resin acids decreases.

The P-values for the other coefficients shown in the Table XII are so large that there is no point in evaluating possible reasons for these coefficients.

Free Fatty Acids

The behaviour of free fatty acids clearly differs from the behaviour of resin acids, see Figure 60. The only similarity between free fatty and resin acids is that when lipase was not used, free fatty acids were not released to the pulp water phase to same extent as were neutral wood resin components. Furthermore, it was observed in the mill measurements, that acidic wood resin was not liberated to the pulp water phase to the same extent as was neutral wood resin. These results could be explained by the fact that resin and free fatty acids are adsorbed to the fibre material in the form of single molecules. This adsorption could be based on the attachment of the fatty acid or resin acid, along with its carboxylate groups, to the acidic groups in the fibre material directly or by with the help of calcium ions. Otherwise, free fatty acids behave in a similar manner to neutral wood resin components.

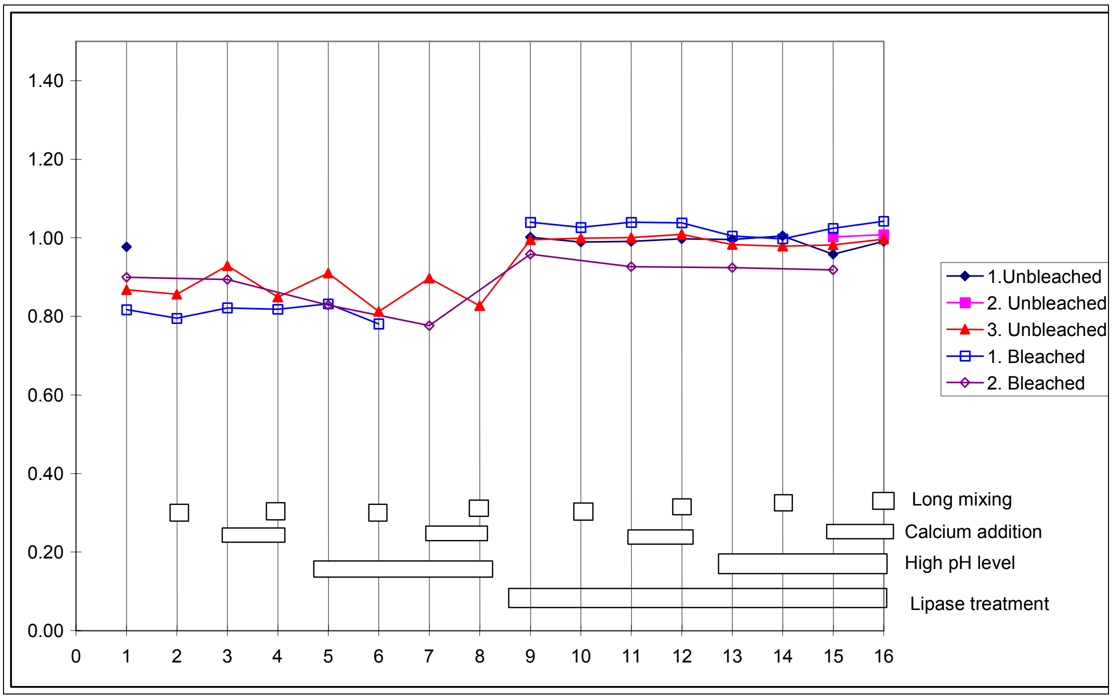


Figure 60. The liberation of free fatty acids to the pulp water phase in relation to the liberation of all wood resin components except resin acids. The results obtained for single experimental points.

Steryl esters

The behaviour of steryl esters does not differ from that of other wood resin components, see Figure 61. The results of the first series, which was obtained for bleached pulp, are clearly below one. The reason for this could be that the steryl ester content measured in the pulp batch, which was used in these experiments, was slightly, approximately 5 %, too high. In the second series, which was obtained for lipase-treated bleached pulp, the results are very high. In addition, the retention of steryl esters at these points is very high, see Figure 62, which indicates that, at these points, the steryl ester content measured in the pulp water phase was too high.

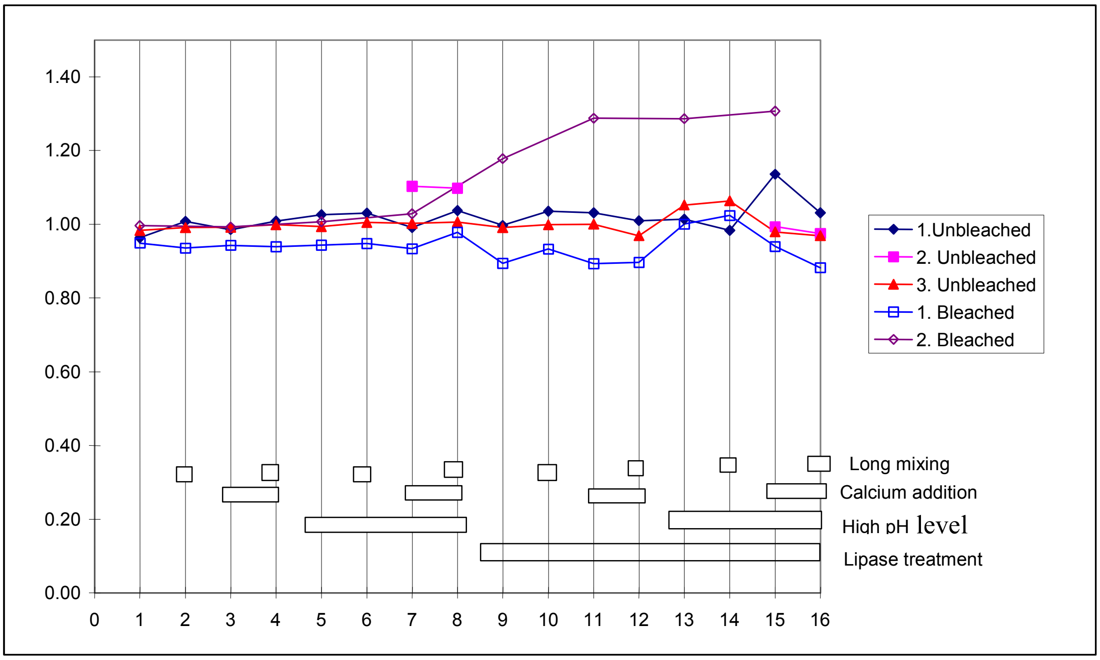


Figure 61. The liberation of steryl esters to the pulp water phase in relation to the liberation of all wood resin components except resin acids. The results were obtained at separate experimental points.

These results indicate that, under the conditions described above, of the major wood resin groups, only resin acids behave in a clearly different manner from the others, which can be explained by the dissolution of resin acids at elevated pH levels.

5.1.3 The Retention of Water-released Wood Resin in Dewatering

In the multivariate experiment was also studied how the different factors affect the retention of water-released wood resin in dewatering. The determination of retention is described in the Chapter 2.3. Retention was measured in the first series for unbleached pulp, as well as in the second series for bleached pulp. The number of experimental points was 26 and all the results are shown in Appendix 9. Table XIII shows the regression model for the retention of water-released wood resin.

Table XIII. The retention of water-released wood resin in dewatering. The table shows the regression coefficients and P values.

R^2 0.58	Regression coefficient	P value
Constant	46	
pH level	-6	0.0034
Bleaching	12	0.0003
Bleaching-lipase	-15	0.0003

As was earlier observed in Chapter 4.3, the pH level has a negative effect on retention.

Bleaching increases the retention of wood resin (12 %). Also, the mill measurements, see Chapter 3.2.3, showed that the retention of wood resin in the press after bleaching (the wash press) was the same or even higher than that in the press before bleaching (the bleach press), although the pH level was clearly higher after bleaching. Peroxide bleaching has a tendency to decrease the freeness value of the pulp [26], which could explain the observed effect of bleaching.

For bleached pulp, lipase treatment had a strong negative effect on the retention of wood resin (-15 %), and the reason for this cross-effect is not known. In chapter 4.4, it was observed that lipase treatment may have a negative effect on the particle size of colloidal wood resin, although this effect was observed only for unbleached pulp.

The regression model for the retention of resin acids in relation to that of all the wood resin components can be seen in Table XIV. The pH level had a strong negative effect on the retention of resin acids, as was expected. In addition, bleaching had a strong negative effect, the reason for which is unknown. Lipase treatment and the addition of calcium increased the relative retention of resin acids at high pH levels. Probably both these factors decreased the dissolution of resin acids. Sihvonen et al. [50] have observed in very similar conditions that the calcium decreases the dissolution of resin acids. Also, in Figure 58, lipase treatment decreased the amount of dissolved resin acids, see experimental point 5 versus 7 and 6 versus 8.

Table XIV. The retention of resin acids in relation to that of all wood resin components. The regression coefficients and P values.

R^2 0.87	Regression coefficient	P value
Constant	0.95	
Bleaching	-0.39	3.20E-06
pH level	-0.58	3.24E-08
pH level-lipase	0.27	0.0014
pH level-calcium	0.19	0.0527

It can be seen in Figure 62 that, for lipase-treated pulp, an increase in the pH level does not decrease the retention of free fatty acids. This result confirms the earlier observation that lipase treatment does not considerably increase the amount of dissolved free fatty acids. Without lipase treatment, the pH level seems to have a negative effect on the retention of free fatty acids, as expected. Otherwise no clear differences in the retention of different wood resin components can be observed in Figure 62. As was mentioned earlier, for lipase-treated bleached pulp, the high retention of steryl esters is caused by the too high analysis results obtained for the steryl esters in the pulp water phase.

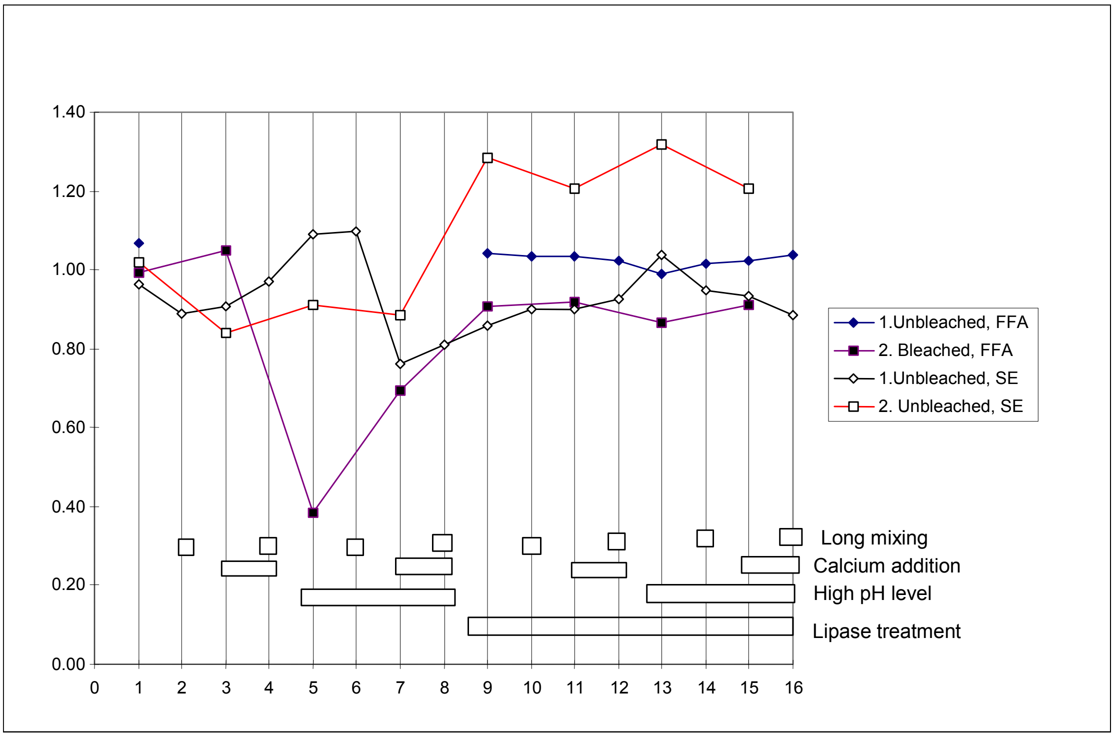


Figure 62. The retention of free fatty acids and steryl esters in relation to that of all the wood resin components except resin acids. The results for separate experimental points.

5.2 Multivariate Experiment II: The Mixing Time, Dewatering Method, pH Level, Lipase Treatment and Temperature

In the second multivariate experiment, the factors studied were the mixing time, dewatering method, pH level, lipase treatment and temperature. The pulp used in this experiment was Pilot-TMP.

Table XV. The factors in the second multivariate experiment. The number of experimental points was 32.

Factor	Level 0	Level 1
1. Mixing time	5 min.	20 min.*
2. Dewatering method	DDJ-dewatering and centrifugation*	Centrifugation of pulp slurry
3. pH level	5*	8
4. Lipase	No*	Yes
5. Temperature	25 °C	60 °C*

*Normally used value

The aim was to obtain reference information on the effects and cross-effects of these factors on the liberation of wood resin to the pulp water phase. The most important verifiable questions were:

1. What is the effect of lipase treatment and its cross-effect with the pH level?
2. What is the effect of the temperature and is it weaker with a longer mixing time as was observed in Figure 20?
3. Does the direct centrifugation of pulp slurry provide smaller results than the normally used procedure of combined DDJ-dewatering and centrifugation as shown in Figure 4?

The structure for the experiments was a two-level five-factorial experiment with 32 experimental points. Two parallel series were obtained, although the wood resin was analysed only from the first series. The turbidity measured from these two series was very similar, which improves the reliability of the obtained results, see Figure 63. The accurate values for the factors and all the numerical results are shown in Appendix 10.

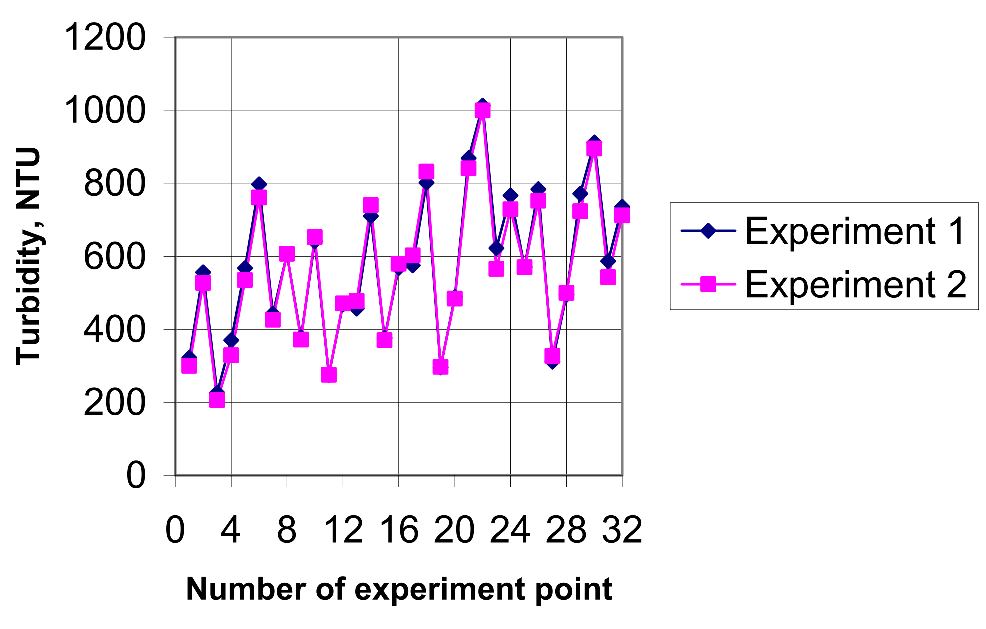


Figure 63. The turbidity measured from the pulp water phase in two parallel experiments.

5.2.1 The Proportion of Wood Resin in the Pulp Water Phase

Table XVI shows the result from the multivariate regression analysis.

Table XVI. The effects and cross-effects of different factors on the proportion of wood resin in the pulp water phase.

R^2 = 98.8 %	Effect, %-units	95 % Interval of confidence, +/- %-units	P-value
Constant	34	3	2.76E-17
Mixing time	24	3	4.25E-15
Dewatering	-11	3	9.64E-09
pH level	22	3	2.56E-13
Lipase	4	3	0.007007
Temperature	23	3	6.64E-13
Mixing-temperature	-6	4	0.002001
Dewatering-temperature	-13	4	1.62E-06
pH level-lipase	-9	4	4.13E-05
Dewatering-pH level-temperature	11	4	1.94E-05

At lower pH levels, lipase treatment had a similar slightly positive effect (4 %) as was also observed in the first multivariate experiment carried out on TMP I. At elevated pH level levels, lipase treatment had a slightly negative effect (pH level-lipase, -9 %). In experiments shown earlier, which were carried out on two different pulp samples at elevated pH levels, similar results were obtained, see Figure 28 and Figure 29. In addition, in the first multivariate experiment carried out on TMP I, lipase had a negative effect under conditions of elevated pH levels, although this was only observed with the addition of calcium, see Table XI. According to these results, the ratio of triglycerides to free fatty acids should not have a significant effect on the liberation of wood resin to the pulp water phase and, thus, natural changes in this ratio or lipase treatment should not have a significant effect on deresination efficiency in practice. Two patent applications [44, 45] provide support for this conclusion, according to which lipase treatment did not exhibit any decreasing effects on the wood resin content of pulp nor in laboratory or mill experiments.

The temperature of the pulp had a stronger positive effect (23 %) than was earlier observed, see Figure 20. In order to ensure the negative cross-effect between mixing and temperature, in accordance with the aim in this experiment, the higher values, used both for the mixing time and temperature, were probably too low. For example, in Figure 20, the distance between the 25- and 60-°C curves does not change notably during the first 20 minutes of mixing. As can be seen in Table XVI, the effect of temperature is weaker for longer mixing times, although the magnitude of this cross-effect is quite small, -6 %. The effect of the mixing time is quite strong, 24 %, and this negative cross-effect can be explained by the simple fact that for longer mixing times, the amount of fibre-bound wood resin in the pulp is smaller, as a result of which the positive effect of temperature should be also smaller.

The direct centrifugation of pulp slurry without normal DDJ dewatering lead to a clearly smaller result (dewatering, -11 %) than expected. Furthermore, at higher temperatures, this difference is much pronounced (dewatering-temperature, -13 %). These results confirm that the direct centrifugation of thick pulp slurry provides too small a result for the wood resin content in the pulp water phase.

5.2.2 Differences in the Liberation of Various Wood Resin Groups to the Pulp Water Phase

Differences in the behaviour of various wood resin groups were studied through the evaluation of how the ratio of one wood resin group to others in the water phase altered.

The following ratios were evaluated
- Resin acids to wood resin
- Steryl esters to the wood resin except resin acids

When the behaviour of steryl esters was evaluated, resin acids were not included in the wood resin because, in this way, the variation caused by the resin acids could be eliminated.

Resin Acids

Table XVII shows the regression model for the ratio of resin acids and Figure 64 the results obtained at different experiment points.

Table XVII. The regression model for the ratio of resin acids.

$R^2 = 98.1$ %	Effect, %-units	95 % Interval of confidence, +/- %-units	P value
Constant	13.0	0.4	
pH level	7.3	0.7	6.24E-17
Lipase	4.5	0.5	3.38E-16
pH level-mixing	-2.4	0.7	1.55E-07
pH level-dewatering	2.4	0.7	1.53E-07
pH level-temperature	-2.0	0.7	4.15E-06

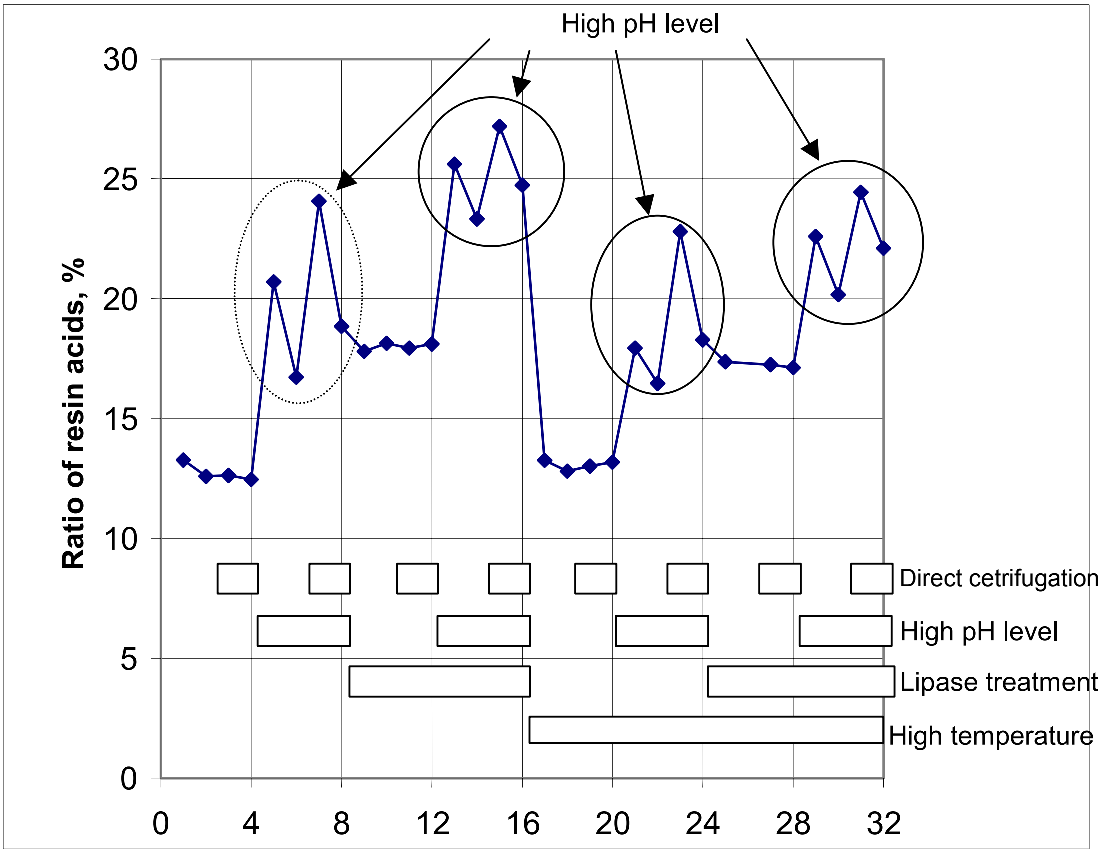


Figure 64. The ratio of resin acids at the different experimental points. Longer mixing times were used at the even-numbered points.

Just like in the first multivariate experiment, the differences in the behaviour of resin acids in relation to that of other wood resin components can be explained solely by the dissolution of resin acids at elevated pH levels and by the effects of different factors on the liberation of colloidal wood resin from the pulp.

When the pH level is low, the proportion of resin acids in the wood resin remains otherwise constant except for the fact that lipase treatment has a positive effect, see Figure 64. As was mentioned earlier in chapter 4.4.2, this is because some long-chain fatty acids, which are liberated from the esterified form during lipase treatment, are located in the same region of the gas chromatogram as resin acids, as a result of which they are erroneously identified as being resin acids.

At elevated pH levels, the proportion of resin acids in the wood resin is larger (Table XVII, pH level 7.3 %) because a part of the resin acids exists in the dissolved state. Also, at elevated pH mixing (-2.4 %), temperature (-2.0) and dewatering (2.4) affect the proportion of resin acids. The reason for this is that the amount of dissolved resin acids remains constant, while mixing and temperature increase and direct centrifugation decrease the amount of colloidal wood resin in the water phase. In that case the ratio of resin acids to all wood resin components behaves in a contrary manner.

Steryl esters

According to Figure 65 and Table XVIII, only lipase treatment alters the behaviour of steryl esters in relation to triglycerides and free fatty acids. However, the explanation for this is the same as in the case of resin acids. Some free fatty acids liberated during lipase treatment are identified as resin acids, which renders the result obtained for free fatty acids too small. This result, for its part, causes the proportion calculated for the steryl esters to be too large.

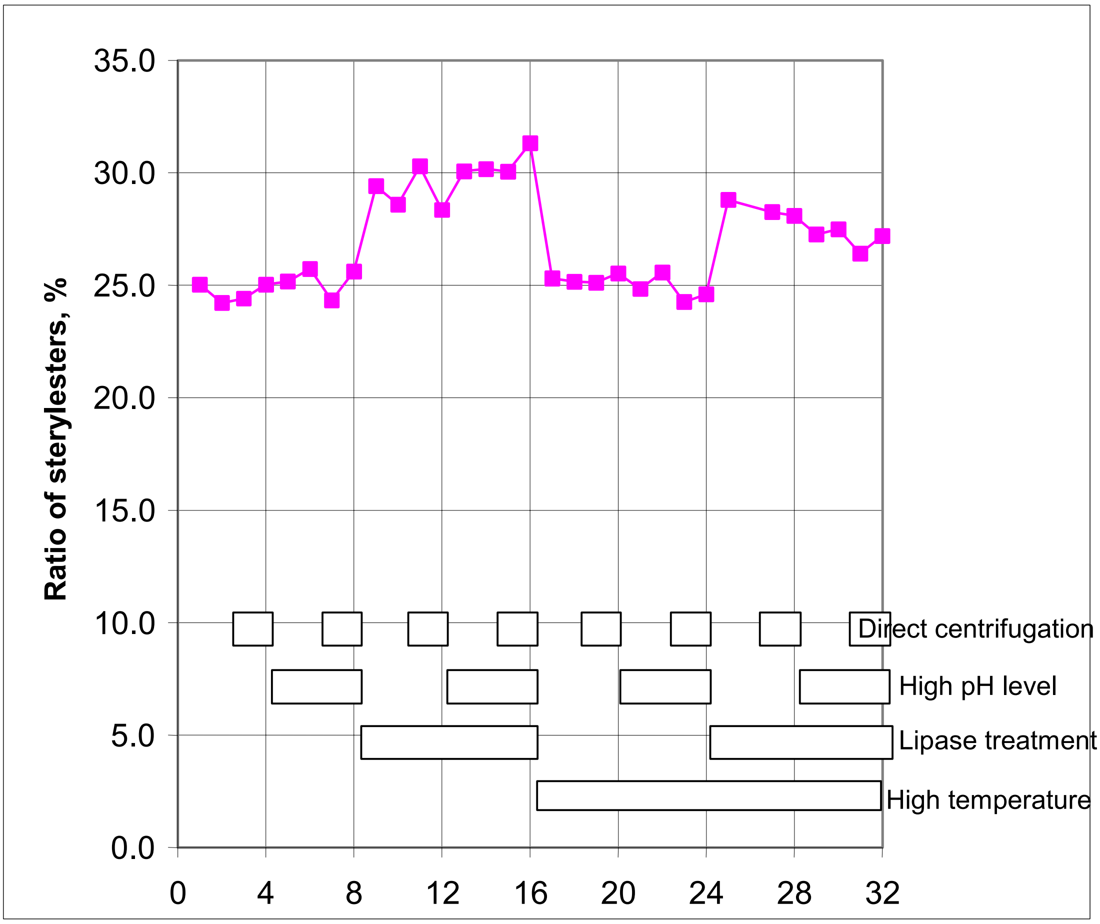


Figure 65. The ratio of steryl esters at different experimental points. Longer mixing times were used at the even-numbered points.

The multivariate regression provides some coefficients that are statistically significant, see Table XVI. In practice, however, these coefficients are too small and complex for them to be evaluated any further.

Table XVIII. The regression model for the ratio of steryl esters.

$R^2 = 96$ %	Effect, %-units	95 % Interval of confidence, +/- %-units	P value
Constant	25	0.3	
Lipase	5	0.5	1.03E-16
Lipase-mixing	-1	0.7	0.00186
Lipase-temperature	-1	0.7	0.002714
Lipase-pH level- temperature	-2	0.9	6.19E-05
Lipase-pH-mixing	2	0.9	0.000139

According to these results, under these conditions, steryl esters, triglycerides and free fatty acids behave similarly, which also confirms that at a pH level of 8, significant amounts of free fatty acids do not exist in the dissolved state.

5.2.3 The Ratio of Turbidity to Wood Resin

Turbidity is commonly used as an indicator for alterations in the concentration of the wood resin in the water phase because of the good correlation between these quantities, see Figure 5. This multivariate experiment also provided information on this correlation and how it is affected by the factors studied here, see Table XIX.

Figure 66 shows that the correlation between turbidity and the concentration of wood resin is rather good. The regression model's R^2 value, which explains the deviation in this correlation, is quite high, 92 %, see Table XIX. This means that a major part of the deviation in the correlation chart, shown in Figure 66, is caused by the factors studied here.

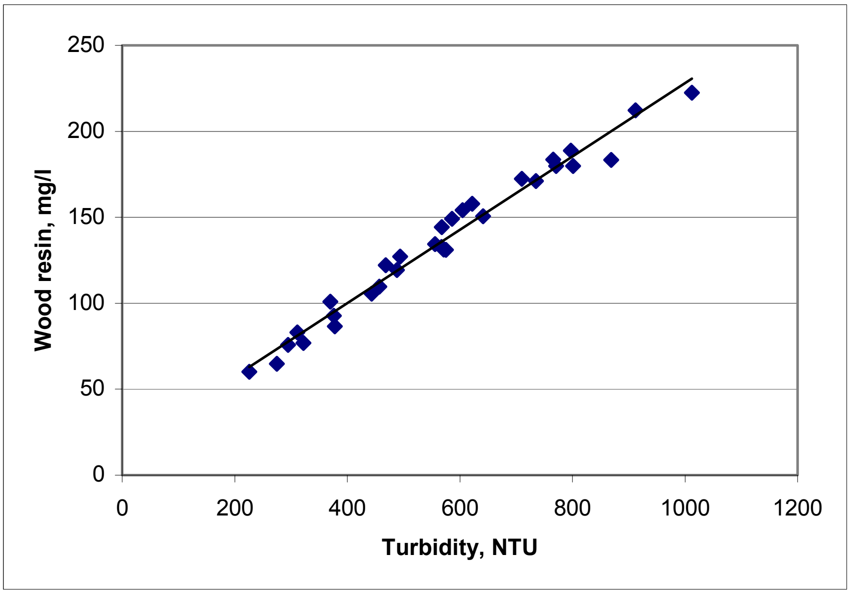


Figure 66. The correlation between turbidity and the wood resin concentration measured from the pulp water phase at different experiment points.

The direct centrifugation reduces the ratio of turbidity to wood resin, (Table XIX, -0.22), which means that the pulp mat formed in centrifugation retains turbidity-causing substances to a larger extent than wood resin does. A similar phenomenon was also observed during dewatering in the mill measurements and laboratory experiments, except that the difference between the behaviour of turbidity and wood resin was even much larger.

Turbidity was measured at room temperature at a pH level of 5. The explanation for the positive effect of the pH level (0.19) and temperature (0.31) is that the increase in temperature and pH level promoted the dissolution of some substances from the pulp. These dissolved substances probably precipitate before turbidity is measured and, thereby, cause additional turbidity.

The number of coefficients in the regression model is high and the cross-effects are complex, which means that the other mechanisms behind these coefficients were very difficult to trace.

Table XIX. The regression model for the ratio of turbidity to wood resin

R^2 = 92 %	Effect	95 % Interval of confidence, +/-	P value
Constant	4.12	0.09	
Dewatering	-0.22	0.12	0.001259
pH level	0.19	0.09	0.00045
Lipase	0.22	0.12	0.001099
Temperature	0.31	0.11	1.52E-05
Dewatering -mixing	-0.22	0.13	0.002229
Temperature-dewatering	-0.40	0.16	5.84E-05
Lipase-pH level	-0.41	0.17	8.71E-05
Lipase-temperature	-0.33	0.17	0.000624
pH level-Lipase-Temperature	0.23	0.19	0.021043
Lipase-dewatering-pH level	0.24	0.15	0.003842
Mixing-dewatering-temperature	0.47	0.18	3.86E-05

6. THE DERESINATION EFFICIENCY IN THE CIRCULATION SYSTEM OF THE MILL

This chapter evaluates the deresination efficiency in the process, how different factors affect deresination efficiency and how it could be improved in practice. This evaluation is carried out with the help of mass balance calculation based on the knowledge obtained in this study on the behaviour of wood resin in the process.

In practice, there exist a lot of different factors that affect the deresination efficiency in the process. Examples of these factors are the amount, quality and point of addition of washing water; the connections of water loops; the nature and existence of bleaching stages; the point at which the filtrate is removed; the freeness value of the pulp; the dewatering technique; the amount and location of dewatering stages and the behaviour of wood resin in the process, which is, to a large extent, determined by the factors listed here. It is impossible to calculate all the possible combinations. Here, the effects of different factors on deresination efficiency was evaluated through the definition of a basic model, with which the effect of individual changes were calculated.

6.1 The Process Layout and the Behaviour of Wood Resin in the Process

Figure 67 shows the process layout including the connections, flows, consistencies and assumed behaviour of wood resin. This kind of process configuration and the behaviour of wood resin would appear to be quite typical.

The model describes a TMP process that produces low-freeness peroxide-bleached pulp. Peroxide bleaching is carried out in one stage at a high consistency, after which comes the washing stage. A total of 8 m^3/o.d.t of washing water is added after bleaching and as make-up water to the clear filtrate chest. The filtrate is removed from the clear filtrate chest, which is quite typical, since in this way, the loss of fibre material is minimised.

The proportion of wood resin liberated to the water phase in the beginning of the process is 55 % and, after bleaching, 50 %. During bleaching, 15 % of the wood resin is degraded. According to the evaluations carried out in Chapter 4.5, the proportions stated here represent rather well real rates of liberation and degradation. The retention rate for the presses was 25 % and was set in accordance with Figure 12 under the assumption that the freeness value of the pulp was 40 ml CSF and that the presses were of the mat-forming type, such as double wire presses, for instance. The average retention rate in the disk filter was 20 % (the retention rates for the cloudy, clear and super-clear filtrate were 15, 20 and 30 %, respectively, whilst the corresponding flow proportions were 50, 30 and 20%, respectively).

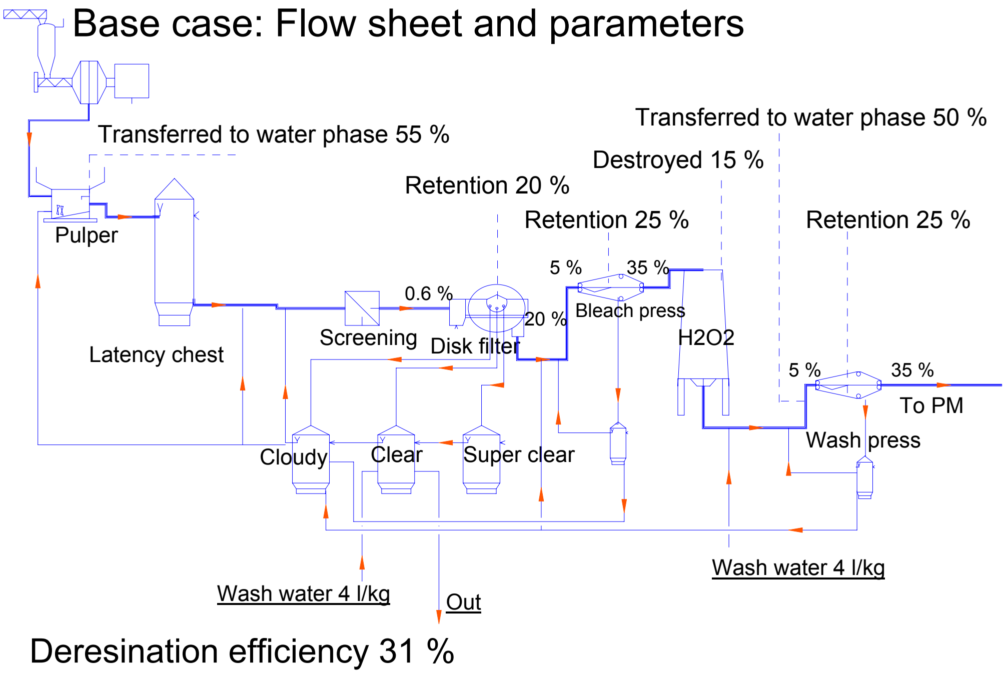


Figure 67. The base case: The flow sheet, consistencies, flows and values of the parameters that describe the behaviour of wood resin in the process.

The biggest source of the error in the mass balance evaluation was related to the effect which the assumed alterations in the process would have on the behaviour of the wood resin in practice. It can be assumed that the proportion of the wood resin degraded during bleaching is not affected by the alterations made to the process. Also, the retention of wood resin during dewatering is determined mainly by the freeness value of the pulp and the dewatering technique employed, as a result of which the other alterations made to the process probably do not affect the retention of wood resin during dewatering.

It is possible that alterations in the water connections and the consumption of water influence the liberation of wood resin from the pulp. After all, according to results shown in chapter 4.9, these effects can be quite weak and complex and, hence, no attempt was made to take these possible effects into account in the mass calculation. For example, were pure water to be used as the washing water, the increase in the consumption of water would, to some extent, have to promote the liberation of wood resin from the pulp, see Chapter 4.9. If the paper machine's white water is used as the washing water, which is quite typical in practice, the relationship between the liberation of wood resin from the pulp and the consumption of water is no longer so clear. In Figure 57 it can be seen that the amount of wood resin liberated from the bleached pulp is smaller when paper machine white water is used as the dilution water than when the filtrate from the wash press is used as the dilution water. This means that an increase in the water intake from the paper machine would decrease the liberation of wood resin from pulp after bleaching.

6.2 The Mass Balance Calculations

In the base case, shown in the Figure 67, the efficiency of deresination is 31 %. This means that the resin content of the pulp that enters the paper machine is 31 % smaller than that of the pulp that enters the process from the refiners. During bleaching, 15 % of the wood resin is degraded, and therefore, the washing efficiency is only 16 %.

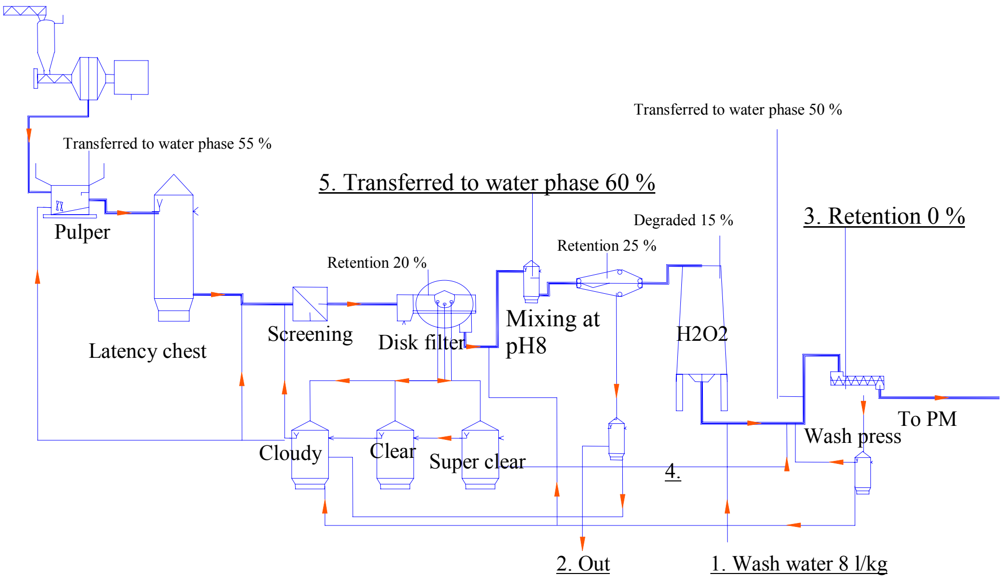
Table XX and Figure 68 shows how different process alterations together, when implemented one after another, can improve deresination efficiency:

1. If all the washing water were introduced to the process after bleaching, the deresination efficiency would increase to 41 %.
2. By removing the filtrate from the bleach press instead of from the clear filtrate chest, it would be possible to achieve a deresination efficiency level of 54 %.
3. If the retention in the wash press was 0 %, the deresination efficiency would be increased to 69 %. This would, in practice, be possible by using a screw press as the wash press, see Chapter 3.3. In such a case, the solid content of the filtrate would be very high, but this would not increase the loss of solid material since the filtrate would not be taken directly out of the process.
4. By using a super-clear filtrate to control the consistency of the pulp in the wash press, deresination efficiency could be further increased to 73 %.
5. In Chapter 4.1 and 4.3 the effect of mixing and the pH level on the liberation of wood resin from the unbleached pulp was quantified. According to these results, the addition, before the bleach press, of a process stage, in which the pulp is mixed thoroughly and the pH level increased from 5 to 8, would make it possible for 60 % of the fibre-bound wood resin to be transferred to the water phase. In such a case, deresination efficiency would increase to 85 %.

Deresination efficiency could still be slightly increased by using screw press as bleach press but in that case lot of fibre material would be lost with the filtrate removed from the process.

Table XX. The effect of individual changes in the process on deresination efficiency, when implemented one after another.

	Deresination efficiency, %
The base case	31
1. All washing water is added after bleaching	41
2. The filtrate is removed from the bleach press	54
3. The retention in the wash press is zero	69
4. Feed consistency is controlled using a super-clear filtrate in the wash press	73
5. pH level is increased to 8 and the pulp is extensively mixed prior to the bleach press -> 60 % of the fibre-bound wood resin is transferred to the water phase	85



1 2 3 4 5
Deresination efficiency 31 -> 41 -> 54 -> 69 -> 73 -> 85 %

Figure 68. Optimal process configuration for the deresination of low freeness mechanical pulp.

This evaluation shows that the efficient deresination of low-freeness mechanical pulp would appear to be possible for an optimal process configuration.

The next two figures illustrate what sort of effects some factors may have on deresination efficiency. The starting point for these calculation was case 2, see Table XX.

Figure 69 shows how the amount of washing water and liberation of wood resin from the pulp after bleaching affect deresination efficiency. When the consumption of water exceeds 10 m^3/o.d.t, deresination is not significantly affected, especially if the liberation of wood resin after bleaching is low. When the liberation of wood resin after bleaching is strong, deresination efficiency increases clearly, also whit higher water usage and when the consumption of water exceeds 15 m^3/o.d.t, a deresination efficiency level of over 70 % is achieved.

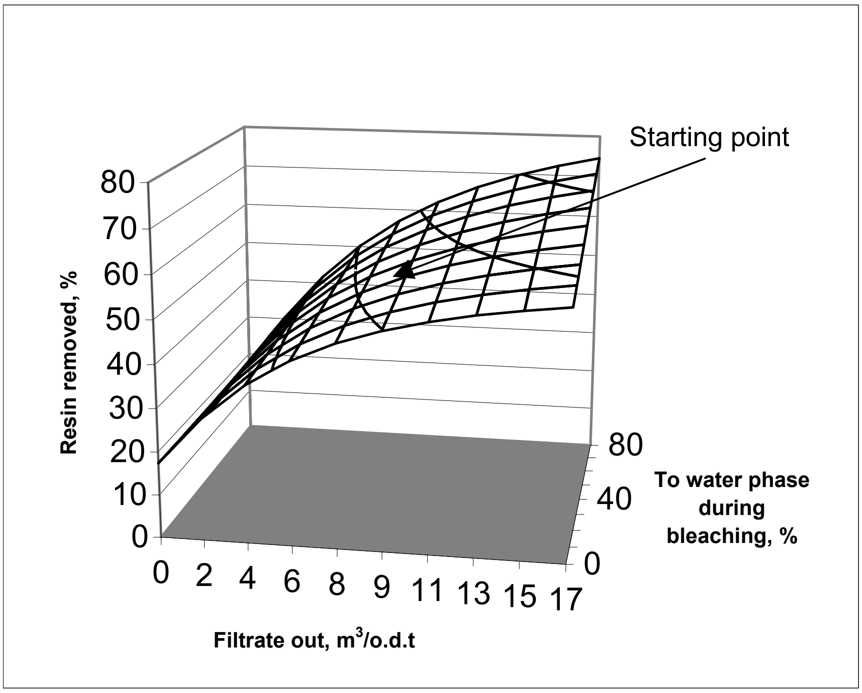


Figure 69. Deresination efficiency as a function of the filtrate removed from the process and the resin transferred to the water phase during bleaching.

Figure 70a shows how the rate of retention and the output consistency in the bleach and wash press affect deresination efficiency. The effect of retention is very strong, whereas that of output consistency is very weak, especially for high rates of retention. At lower levels of water consumption, see Figure 70b, the effects of both output consistency and retention are stronger than at higher levels of water consumption, see Figure 70a. When the retention rate is 0 % and output consistency 45 %, deresination efficiency is not greatly reduced when the removal of the filtrate from the process is reduced from 8 to 4 m3/o.d.t.

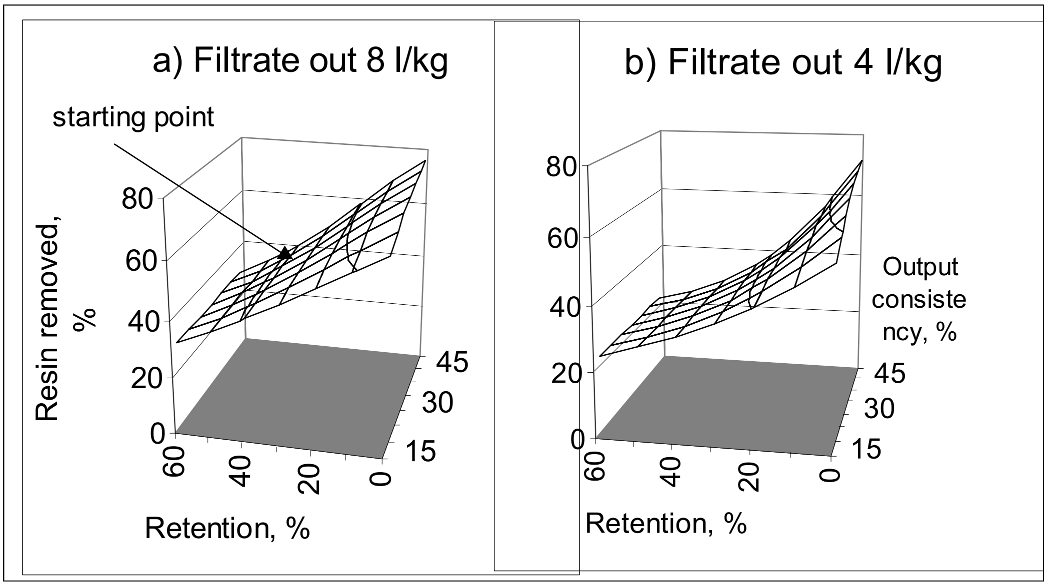


Figure 70. Deresination efficiency as a function of retention and output consistency in presses at two different levels of water consumption.

7. SUMMARY AND CONCLUSIONS

In this thesis was studied the behaviour of wood resin in the production of mechanical pulp. The main objective was to produce information for the estimation of the flow balance of wood resin in mechanical pulping and to show what kinds of possibilities there exist for the improvement of deresination efficiency.

It was observed that chemical alterations occur in the wood resin only during peroxide bleaching, a significant amount of water-released wood resin is retained in the pulp mat during dewatering and the amount of wood resin in the solid phase of the process filtrates is very small. On the basis of this information, it was concluded that there exist three parameters that are related to the behaviour of wood resin and that determine the flow balance in the process. These parameters are listed below:

1. The liberation of wood resin to the pulp water phase
2. The retention of water-released wood resin during dewatering
3. The proportion of wood resin degraded in peroxide bleaching

The effects of different factors on these parameters as well as the basic mechanisms behind these effects were evaluated in this thesis. In addition, this study produced information related to the values of these parameters in the existing processes. This information was used in mass balance calculations for evaluating the deresination efficiency as well as the effects of different factors on the deresination efficiency in a pulping plant that produces low-freeness mechanical pulp.

The quantities of the chemical and phase alterations of the wood resin in the process were estimated on the basis of mill measurements, laboratory experiments and reference information obtained from literature. The proportion of the wood resin liberated to the water phase before peroxide bleaching was found to be about 50 % and the information obtained indicated that this ratio would not differ considerably between different cases. After bleaching about 50 % of the remaining fibre-bound wood resin was found to have been liberated to the water phase. A large deviation in this ratio was observed between separate laboratory studies and the reason for it remained unclear. The initial pH level in bleaching had a clear effect on the liberation of wood resin from the pulp. During peroxide bleaching, about 15 % of the wood resin is degraded and the bleaching conditions did not influence this ratio. In the mill measurements, no other significant chemical or phase alterations were observed in the wood resin.

In mat-forming dewatering devices, water-released wood resin is significantly retained in the fibre mat. The freeness value of the pulp had a significant effect on retention in this case. In the roll press, the rate of retention was found to be higher and in the disk filter lower than in the wire press. In screw press dewatering, the predominant phenomenon instead of retention was the dispersion of fibre-bound wood resin to the pulp water phase. The pH level did not affect the retention of neutral wood resin during dewatering, although it decreased the retention of acidic wood resin and mainly that of resin acids. However, this negative effect was quite weak from the practical point of view.

The influence of the mixing time and intensity on the liberation of wood resin from pulp was quantified in laboratory experiments. These results were in good agreement with the finding that, in the process, mixing prior to peroxide bleaching was not adequate for the liberation of wood resin from the pulp. Additional mixing did not lead to the liberation of wood resin in the pulp samples taken from the process after peroxide bleaching. The effects of mixing and temperature were closely linked to each other. At increased temperatures, wood resin was more easily liberated from the pulp, but when the pulp was extensively mixed, the effect of temperature on the rate of liberation was less pronounced.

It was concluded that a change in the pH level from 5 to 8 increases the liberation of wood resin by about 10 to 20 percentage units. Also, it was assumed that this positive effect is at least partly due to the dissociation of acidic wood polymers which then increases the anionic charge of the colloidal and fibre material.

The degree of refining did not have any effect on the liberation of wood resin or the different components of wood resin to the pulp water phase. It was concluded that, in pulp, which has a rather high freeness value, 500 ml CSF, the parenchyma cells are damaged to an extent that makes all the wood resin located in these cells accessible for liberation to the pulp water phase. It was also concluded that the degree of refining does not affect the adsorption of wood resin to the pulp.

The use of dispersing agents was found to increase the liberation of wood resin to the pulp water phase significantly only in a system where this liberation was limited by the presence of calcium.

It was concluded that the following properties of the dilution water influence the liberation of wood resin to the pulp water phase: the electrolyte and wood resin concentration, the buffer capacity and the amount of dissolved wood polymers. The effect of wood resin and electrolytes is negative and dissolved wood polymers weaken the negative effect of electrolytes. However, in the practice, only dramatic changes in the quality of the dilution water may have a notable effect on the liberation of wood resin to the pulp water phase.

Depending on the conditions, the use of lipase had both positive as well as negative effects on the liberation of wood resin from pulp. These effects were quite weak, as a result of which at present, it seems that lipase treatment cannot be used for improving deresination efficiency in practice. This result also indicates that the ratio of neutral wood resin to free fatty acids does not significantly affect the deresination efficiency in the process.

In several mill measurements and laboratory experiments, it was observed that, for unbleached pulp, acidic wood resin was not liberated to the pulp water phase to the same extent as was neutral wood resin and, for peroxide-bleached pulp, this difference was even larger. Also, the multivariate experiments showed that lipase treatment had a negative effect on the liberation of wood resin from the pulp for peroxide-bleached pulp if the pH level was high and especially if the pH level was high and calcium was added to the pulp. These observations could be due to the formation of insoluble calcium soaps or the fact that resin and free fatty acids are adsorbed to the fibre material in the form of single molecules. This adsorption might be based on the attachment of the fatty or resin acid, along with its carboxylate groups, to the acidic groups in the fibre material directly or with the aid of calcium ions.

Otherwise, no other differences, except in the case of resin acids, were observed in the liberation of different wood resin components to the pulp water phase. These differences could be explained by the dissolution of resin acids at elevated levels of pH. The results support the assumption that the wood resin colloids, formed in refining, are chemically homogeneous.

The increasing effect of bleaching on the liberation of wood resin from the pulp was assumed to be caused by an increase in the charge of the fibre material, which would lead to an increase in the repulsion between the fibre material and colloidal wood resin. The same assumption could be used to explain the observation that, for unbleached pulp, the fibre material enhanced the calcium-induced destabilisation of wood resin, whereas for bleached pulp, it did not. This result also indicates that the destabilisation mechanism of wood resin for bleached pulp may differ from that for unbleached pulp. For unbleached pulp, the destabilisation mechanism is most probably an attachment of the wood resin to the fibre material, but for bleached pulp it is more likely to be the agglomeration of wood resin.

It was observed that, for unbleached pulp, the effect of the addition of calcium on the destabilisation of wood resin depends strongly on the concentration of the dissolved and colloidal substances in the pulp, but, for peroxide-bleached pulp, this kind of effect does not exist. This difference was explained by the presence of dissolved galactoglucomannans in unbleached pulp and the deacetylation of these galactoglucomannans during peroxide bleaching.

According to the computational analysis, the wood resin content of low-freeness mechanical pulp can be reduced significantly if the process contains a peroxide bleaching and a subsequent washing stage. In the case of optimal process configuration, it appears possible to achieve a deresination efficiency level as high as 85 % at a water consumption level of 8 m^3/o.d.t.

The analytical approach and reference information related to the behaviour of wood resin, as presented in this thesis, provide a good basis for the evaluation of the flow balance of wood resin in a mechanical pulping plant. These kinds of evaluations are necessary, for instance, when predicting how different process alterations or possible alterations in the behaviour of wood resin will affect deresination efficiency in practice.

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LIST OF APPENDICES

Appendix 1

The process flows and consistencies in the mill survey in February 2000.

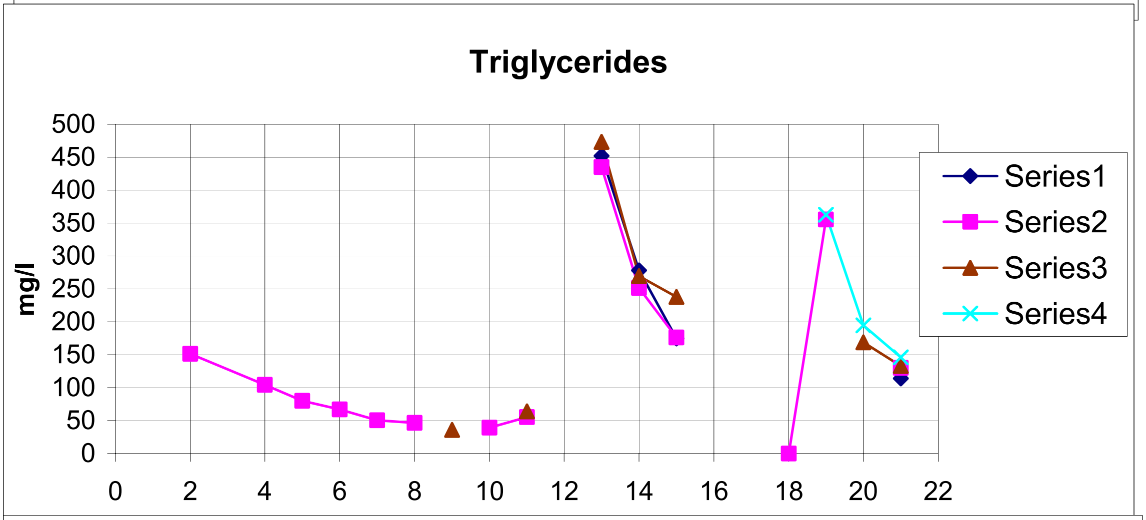
Production	Adt/d
TMP	864
Bleached TMP	205

	Flows	l/s
In	Pure water to clear filt. chest	7
	PM circ. water to clear filt. chest	45
	Pure water to bleaching	0.5
	PM circ. water after bleaching	4
Out	Clear filtrate out	26
	Super clear filtrate out	20
	Bleach press filt. chest out	0
	Wash press filt. chest out	5
Inside	Bleach press shower water	32
	Wash press shower water	20

No.	Consistency	%
1	After II-Refiner	40
2	Pulper, 4 %	4.7
4	Latency chest, 2 %	2.0
5	Before screening	1.1
6	Disck filter feed	0.6
12	Discfilter out	19.0
13	Bleache press feed	9.3
16	Bleaching in	37.0
17	Bleaching out	34.3
19	Wash press feed	9.4
22	Wash press out	30

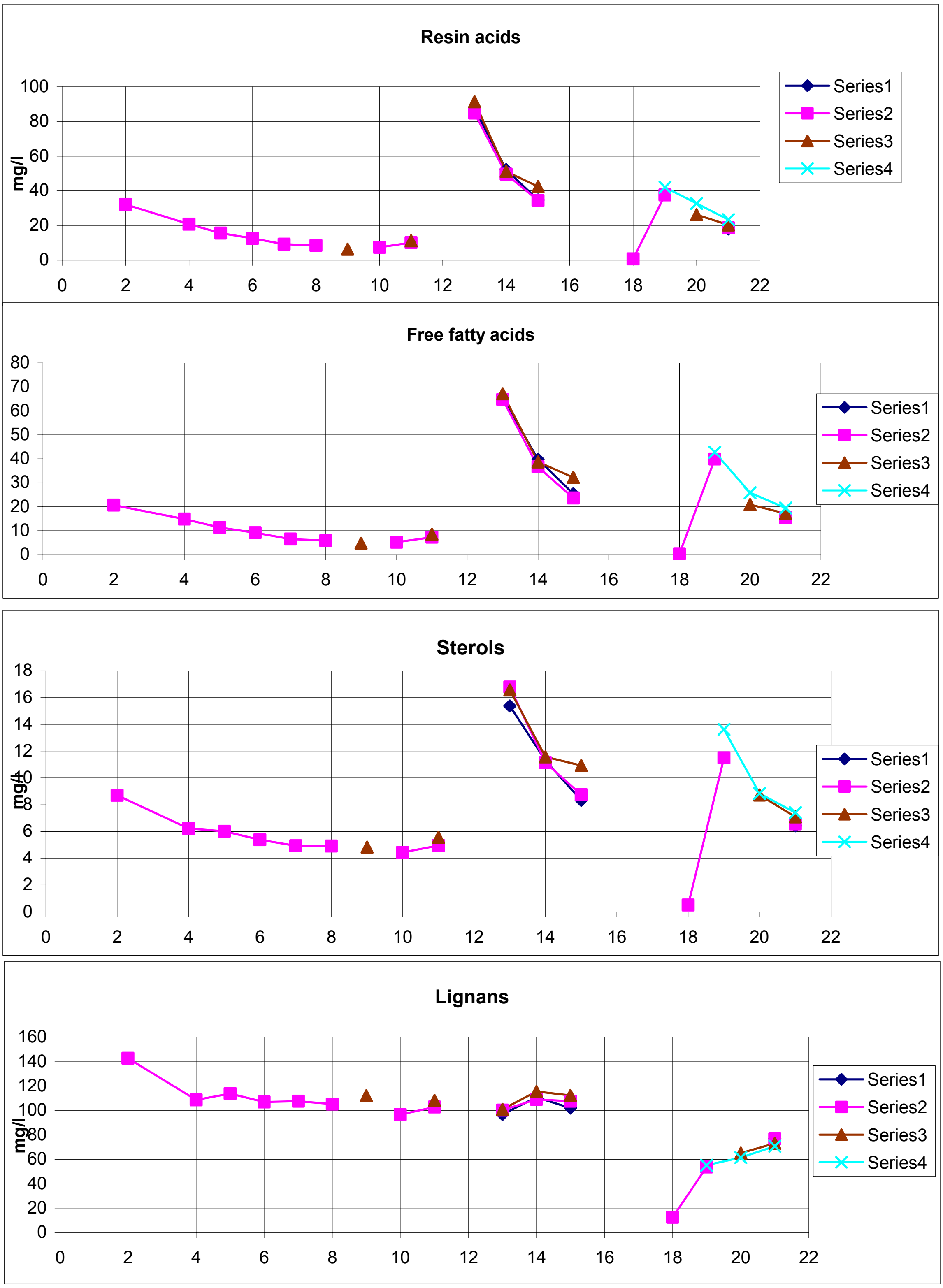
	Solids content	mg/l
7	Cloudy filtrate	150
8	Clear filtrate	50
9	Super clear filtrate	10
10	Clear filtrate chest	40
11	Cloudy filtrate chest	97
14	Bleach press filtrate	400
15	Bleach press filt. chest	289
20	Wash press filtrate	400
21	Wash press filt. chest	226

The results of water-released wood resin in the mill survey in February 2000.



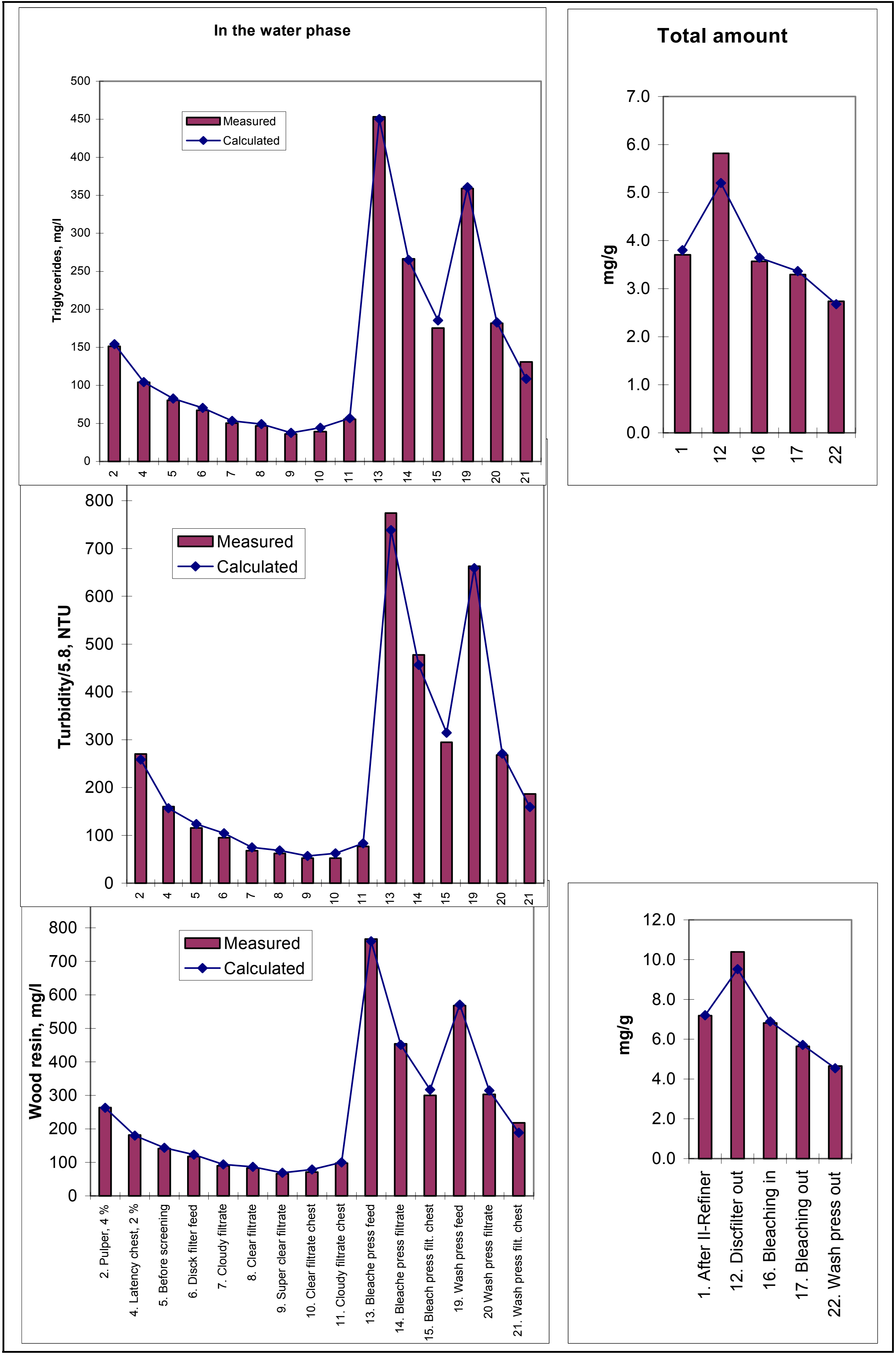
Appendix 2/2

The results of water-released wood resin in the mill survey in February 2000.



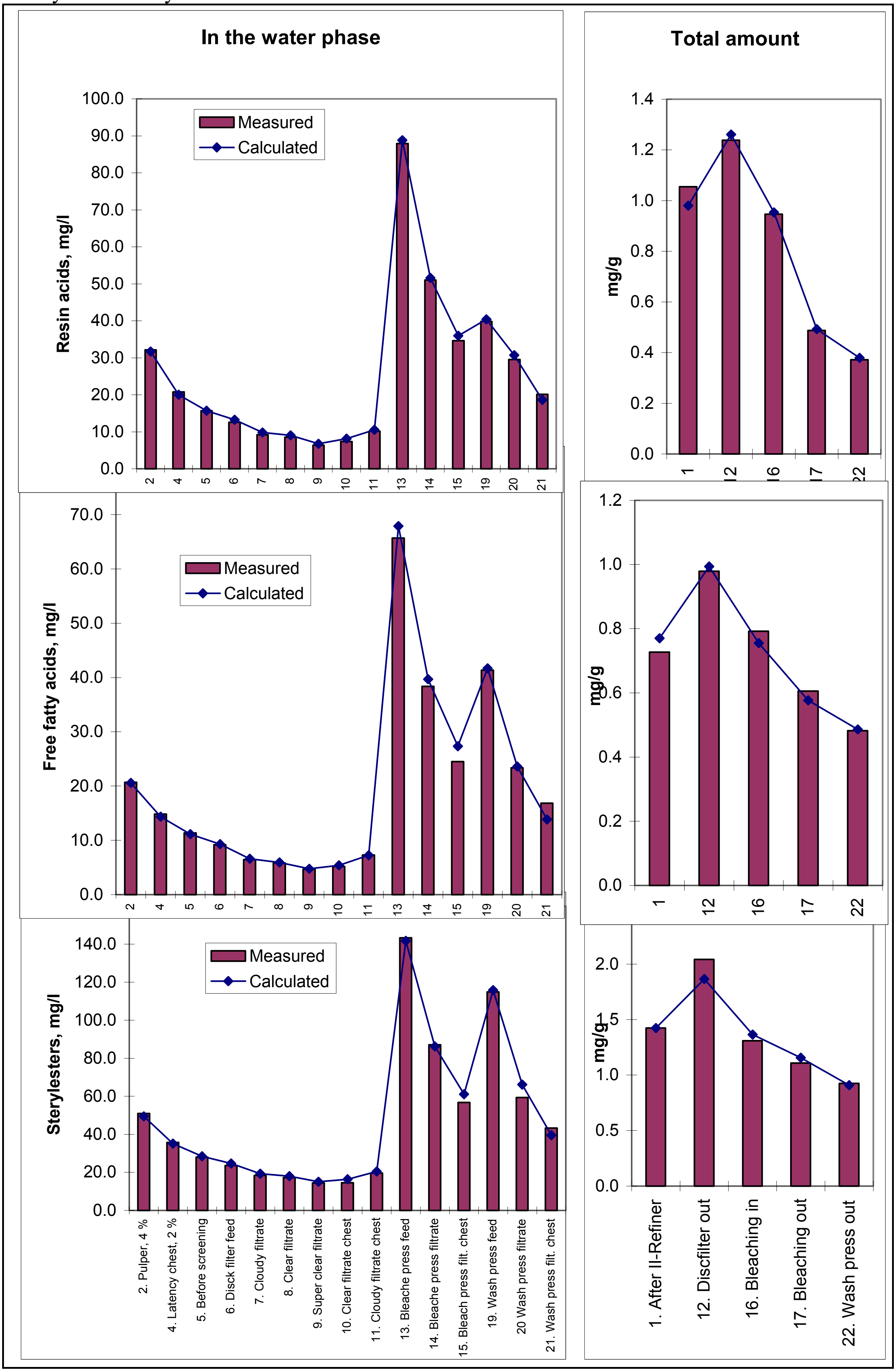
Appendix 3/1

The measured and calculated values for turbidity and different wood resin groups in the mill survey in February 2000.

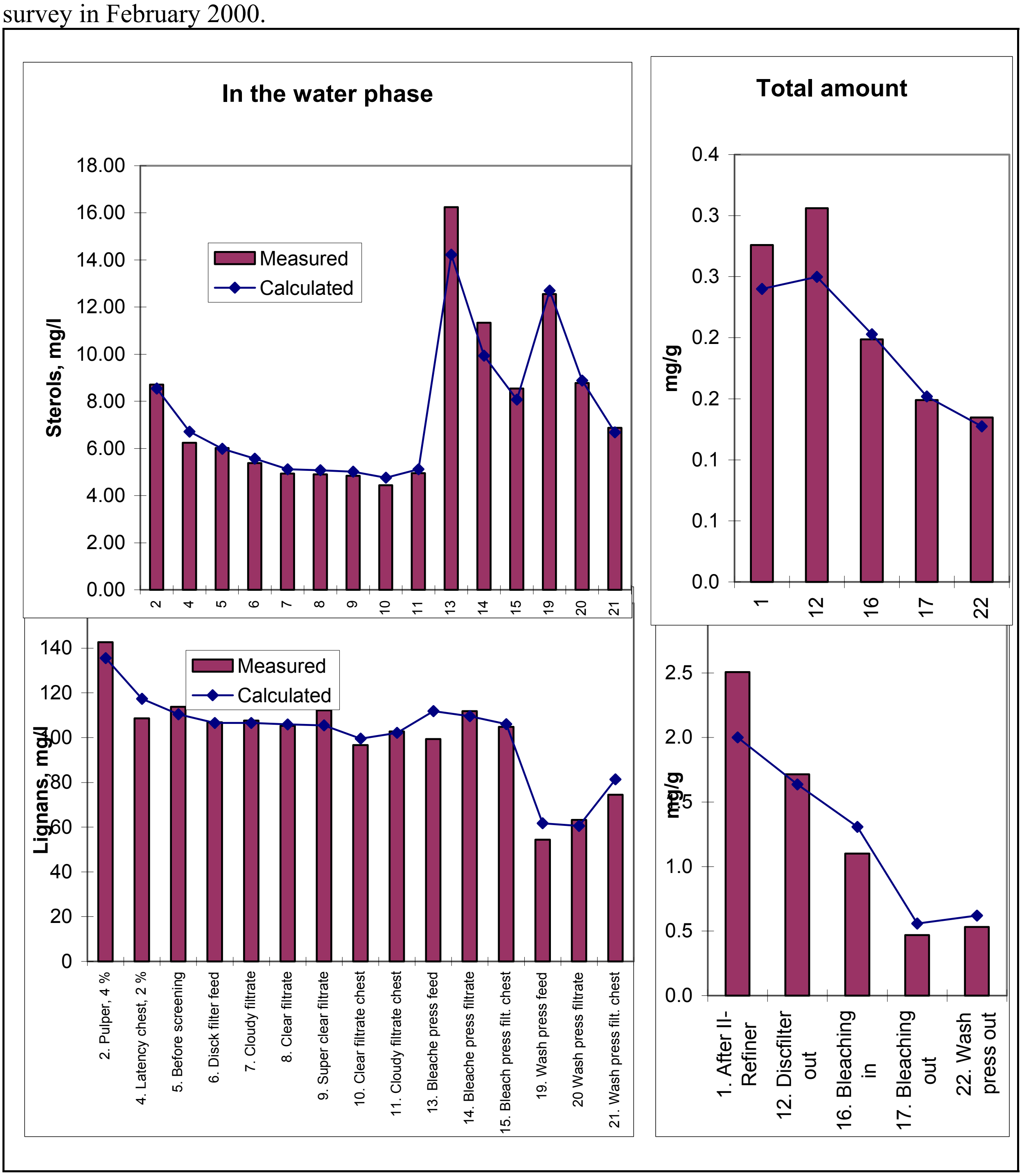


Appendix 3/2

The measured and calculated values for turbidity and different wood resin groups in the mill survey in February 2000.



The measured and calculated values for turbidity and different wood resin groups in the mill survey in February 2000.



The results from the earlier mill measurement carried out in August 1998.

Production	Adt/d
TMP	620
Bleached TMP	328

	Flows	l/s
In	Pure water to clear filt. chest	7
	PM circ. water to clear filt. chest	45
	Pure water to bleaching	0.5
	PM circ. water after bleaching	19
Out	Cloudy filtrate out	30
	Super clear filtrate out	0
	Bleach press filt. chest out	0
	Wash press filt. chest out	15
Inside	Bleach press shower water	8
	Wash press shower water	6

No.	Consistency	%
1	After II-Refiner	55
2	Pulper, 4 %	4.7
4	Latency chest, 2 %	2.1
5	Before screening	1.0
6	Disck filter feed	0.6
12	Discfilter out	16.0
13	Bleache press feed	8.3
16	Bleaching in	36.0
17	Bleaching out	34.4
19	Wash press feed	7.7
22	Wash press out	35

No.	Solids content	mg/l
7	Cloudy filtrate	150
8	Clear filtrate	50
9	Super clear filtrate	10
10	Clear filtrate chest	40
11	Cloudy filtrate chest	95
14	Bleach press filtrate	400
15	Bleach press filt. chest	389
20	Wash press filtrate	400
21	Wash press filt. chest	380

The results from the earlier mill measurement carried out in August 1998.

In the water phase, mg/l

		Measured	Calculated	Difference, %	Measured	Calculated	Difference, %
	Sample	**Wood resin**			**Turbidity/5.8**		
2	Pulper, 4 %	271	255	6.0	258	266	-3.3
4	Latency chest, 2 %	195	186	4.4	168	178	-5.7
6	Disck filter feed	149	147	1.6	109	130	-18.7
7	Cloudy filtrate	129	127	1.4	91	108	-19.1
8	Clear filtrate	125	123	1.4	87	103	-18.8
9	Super clear filtrate	111	109	1.4	66	78	-17.8
13	Bleache press feed	572	585	-2.3	624	610	2.2
14	Bleach press filtrate	425	435	-2.4	397	388	2.2
19	Wash press feed	518	516	0.3	533	532	0.1
20	Wash press filtrate	386	385	0.3	359	359	0.1
	Sample	**Triglycerides**			**Sterylesters**		
2	Pulper, 4 %	143	140	2.0	69	68	1.3
4	Latency chest, 2 %	100	101	-0.7	53	51	4.0
6	Disck filter feed	80	79	0.7	38	42	-11.1
7	Cloudy filtrate	66	66	0.4	35	39	-11.6
8	Clear filtrate	66	66	0.2	33	37	-12.7
9	Super clear filtrate	56	56	0.9	30	34	-12.3
13	Bleache press feed	282	340	-20.6	142	131	8.0
14	Bleach press filtrate	211	255	-20.6	104	96	7.9
19	Wash press feed	287	287	0.2	156	141	9.6
20	Wash press filtrate	219	218	0.3	106	96	9.4
	Sample	**Free fatty acids**			**Resin acids**		
2	Pulper, 4 %	12	13	-5.2	42	42	-0.6
4	Latency chest, 2 %	9	9	-0.3	29	30	-3.8
6	Disck filter feed	6	6	-0.6	23	23	-2.0
7	Cloudy filtrate	4	4	-0.2	20	21	-3.3
8	Clear filtrate	5	5	-1.7	18	18	-1.7
9	Super clear filtrate	4	4	6.4	16	17	-3.4
13	Bleache press feed	34	34	0.8	98	96	2.0
14	Bleach press filtrate	25	24	2.5	74	72	2.1
19	Wash press feed	15	15	1.7	40	40	0.2
20	Wash press filtrate	12	12	-4.2	36	36	-0.9
	Sample	**Sterols**			**Lignans**		
2	Pulper, 4 %	6	5	18.6	263	260	1.1
4	Latency chest, 2 %	3	4	-21.7		227	
6	Disck filter feed	4	4	-7.9	210	209	0.5
7	Cloudy filtrate	3	4	-7.9	210	209	0.5
8	Clear filtrate	3	3	-7.9	207	209	-1.0
9	Super clear filtrate	3	3	-7.9	202	209	-3.5
13	Bleache press feed	15	15	-0.4	190	205	-7.9
14	Bleach press filtrate	11	11	-0.4	184	201	-9.3
19	Wash press feed	19	19	0.7	55	51	7.4
20	Wash press filtrate	15	15	0.7	52	50	4.1

Total amount mg/o.d.g

		TG	SE	FFA	RA	SE	Wood res.	LIGN
1	After II-Refiner	2.94	1.33	0.43	1.32	0.5	**6.5**	3.5

Appendix 5

The results from the later mill measurement carried out in August 2000.

Process flows and consistencyes

	Production	Adt/d
	TMP	609
	Bleached TMP	267

	Flows	l/s
In	Pure water to clear filt. chest	5
	PM circ. water to clear filt. chest	69
	Pure water to bleaching	0.5
	PM circ. water after bleaching	5
Out	Clear filtrate out	38
	Super clear filtrate out	30
	Bleach press filt. chest out	0
	Wash press filt. chest out	5
Inside	Bleach press shower water	32
	Wash press shower water	20

No.	Consistency	%
1	After II-Refiner	40
2	Pulper, 4 %	4.7
4	Latency chest, 2 %	2.1
5	Before screening	1.1
6	Disck filter feed	0.6
12	Discfilter out	19.0
13	Bleache press feed	9.2
16	Bleaching in	37.0
17	Bleaching out	34.9
19	Wash press feed	7.6
22	Wash press out	30

No.	Solids content	mg/l
7	Cloudy filtrate	150
8	Clear filtrate	50
9	Super clear filtrate	10
10	Clear filtrate chest	40
11	Cloudy filtrate chest	97
14	Bleach press filtrate	400
15	Bleach press filt. chest	295
20	Wash press filtrate	400
21	Wash press filt. chest	278

Wood resin analyses

No	Samples	TG	SE	FFA	RA	ST	**Wood resin**	LIGN
	Water samples, mg/l							
9	Clear filtrate chest	19	13	5	7	3	**47**	119
15	Bleach press filt. chest	88	44	28	30	8	**198**	109
21	Wash press filt. chest o	74	36	19	21	7	**157**	79
	Pulp samples, mg/o.d.g							
1	After II-Refiner	2.1	1.2	1.2	1.2	0.3	**5.9**	2.6
17	Bleaching out	2.2	1.1	0.9	0.6	0.2	**5.0**	0.8

Multivariate experiment I; the values used in the regression analyses.

						Level 0	Unbleached	5 min	0 mM	5	No
	Proportion in the		Proportion in the water phase			**Level 1**	Bleached	10 min	2 mM	8	Yes
	Water phase, %		in relation to others								
No	Wood resin		RA/Wood res.	SE/(Wood res.-RA)	FFA/(Wood res.-RA)		Bleaching	Mixing	CaCl2	pH	Lipase
1	**63**		**0.90**	**0.96**	**0.98**		0	0.1	0.0	0.0	0
2	**57**		**0.91**	**1.01**			0	1.0	0.0	0.0	0
3	**57**		**0.89**	**0.99**			0	0.1	0.4	-0.1	0
4	**47**		**0.90**	**1.01**			0	1.0	0.4	-0.1	0
5	**70**		**1.12**	**1.03**			0	0.1	0.0	1.0	0
6	**76**		**0.97**	**1.03**			0	1.0	0.0	1.0	0
7	**60**		**0.96**	**0.99**			0	0.1	0.4	0.7	0
8	**66**		**0.94**	**1.04**			0	1.0	0.4	0.7	0
9	**62**		**0.95**	**1.00**	**1.00**		0	0.1	0.0	0.1	1
10	**63**		**0.99**	**1.04**	**0.99**		0	1.0	0.0	0.1	1
11	**48**		**1.00**	**1.03**	**0.99**		0	0.1	0.4	-0.1	1
12	**56**		**0.98**	**1.01**	**1.00**		0	1.0	0.4	-0.1	1
13	**80**		**1.13**	**1.01**	**1.00**		0	0.1	0.0	1.1	1
14	**77**		**1.04**	**0.98**	**1.01**		0	1.0	0.0	1.1	1
15	**57**		**1.11**	**1.14**	**0.96**		0	0.1	0.4	0.7	1
16	**67**		**1.04**	**1.03**	**0.99**		0	1.0	0.4	0.7	1
17	**59**		**0.97**	**1.07**			0	0.5	0.2	0.3	0
18	**63**		**1.01**	**1.05**	**0.98**		0	0.5	0.2	0.3	1
7	**63**		**1.04**	**1.10**			0	0.1	0.4	1.0	0
8	**62**		**1.03**	**1.10**			0	1.0	0.4	1.0	0
15	**60**		**1.08**	**0.99**	**1.00**		0	0.1	0.4	1.1	1
16	**65**		**1.04**	**0.97**	**1.01**		0	1.0	0.4	1.1	1
17	**56**		**0.97**	**1.03**			0	0.5	0.2	0.5	0
18	**64**		**1.02**	**1.07**	**0.98**		0	0.5	0.2	0.5	1
1	**56**		**0.93**	**0.98**	**0.87**		0	0.0	0.0	-0.1	0
2	**62**		**0.89**	**0.99**	**0.86**		0	1.0	0.0	-0.1	0
3	**36**		**0.94**	**0.99**	**0.93**		0	0.0	1.0	-0.2	0
4	**47**		**0.90**	**1.00**	**0.85**		0	1.0	1.0	-0.2	0
5	**68**		**1.22**	**0.99**	**0.91**		0	0.0	0.0	0.9	0
6	**74**		**1.03**	**1.00**	**0.81**		0	1.0	0.0	0.9	0
7	**49**		**1.20**	**1.00**	**0.90**		0	0.0	1.0	0.7	0
8	**58**		**0.95**	**1.01**	**0.83**		0	1.0	1.0	0.7	0
9	**54**		**0.97**	**0.99**	**1.00**		0	0.0	0.0	0.0	1
10	**67**		**0.96**	**1.00**	**1.00**		0	1.0	0.0	0.0	1
11	**47**		**1.01**	**1.00**	**1.00**		0	0.0	1.0	-0.1	1
12	**55**		**0.98**	**0.97**	**1.01**		0	1.0	1.0	-0.1	1
13	**67**		**1.18**	**1.05**	**0.98**		0	0.0	0.0	0.9	1
14	**76**		**1.02**	**1.06**	**0.98**		0	1.0	0.0	0.9	1
15	**43**		**1.12**	**0.98**	**0.98**		0	0.0	1.0	0.7	1
16	**60**		**1.01**	**0.97**	**1.00**		0	1.0	1.0	0.7	1
17	**62**		**0.98**	**1.00**	**0.84**		0	0.5	0.5	0.6	0
18	**72**		**1.00**	**0.99**	**1.00**		0	0.5	0.5	0.6	1
1	**67**		**1.05**	**0.95**	**0.82**		1	0.0	0.0	0.1	0
2	**77**		**1.02**	**0.94**	**0.79**		1	1.0	0.0	0.1	0
3	**61**		**1.05**	**0.94**	**0.82**		1	0.0	1.0	0.1	0
4	**74**		**0.98**	**0.94**	**0.82**		1	1.0	1.0	0.1	0
5	**85**		**1.41**	**0.94**	**0.83**		1	0.0	0.0	1.3	0
6	**96**		**1.23**	**0.95**	**0.78**		1	1.0	0.0	1.3	0
7	**75**		**1.40**	**0.93**	**1.11**		1	0.0	1.0	1.2	0
8	**89**		**1.21**	**0.98**	**1.14**		1	1.0	1.0	1.2	0
9	**57**		**1.41**	**0.89**	**1.04**		1	0.0	0.0	0.0	1
10	**68**		**1.35**	**0.93**	**1.03**		1	1.0	0.0	0.0	1
11	**51**		**1.45**	**0.89**	**1.04**		1	0.0	1.0	0.0	1
12	**66**		**1.46**	**0.90**	**1.04**		1	1.0	1.0	0.0	1
13	**79**		**1.28**	**1.00**	**1.00**		1	0.0	0.0	1.1	1
14	**94**		**1.14**	**1.02**	**1.00**		1	1.0	0.0	1.1	1
15	**61**		**1.40**	**0.94**	**1.02**		1	0.0	1.0	1.1	1
16	**76**		**1.22**	**0.88**	**1.04**		1	1.0	1.0	1.1	1
17	**83**		**1.10**	**0.97**	**0.84**		1	0.5	0.5	0.6	0
18	**71**		**1.26**	**1.01**	**1.00**		1	0.5	0.5	0.5	1
1	67.0		0.71	1.00	0.90		1	0	0	0.1	0
3	61.2		0.80	0.99	0.89		1	0	1	0.0	0
5	83.0		1.04	1.01	0.83		1	0	0	1.4	0
7	75.1		0.88	1.03	0.78		1	0	1	1.3	0
9	58.8		1.00	1.18	0.96		1	0	0	0.1	1
11	51.4		0.91	1.29	0.93		1	0	1	0.0	1
13	66.0		1.06	1.29	0.92		1	0	0	1.2	1
15	50.7		1.13	1.31	0.92		1	0	1	1.2	1
No	Wood resin		HH/rasval	sterest/rasval-HH	RH/rasval-HH		Bleaching	Mixing	CaCl2	pH	Lipase

Appendix 7

Multivariate experiment I; the wood resin concentration in the filtrates and the original values of the variables.

	No	FFA	RA	SE	TG	Wood resin mg/l	H2O2-bleaching	Mixing min	CaCl2-addition mM	pH	Lipase
1. Unbleached	1	37	37	44	123	**241**	0	10	0	5	0
	2	74	37	42	65	**217**	0	90	0	5	0
	3	112	38	40	26	**216**	0	10	0.83	4.8	0
	4	95	32	34	19	**179**	0	90	0.83	4.8	0
	5	98	57	49	62	**266**	0	10	0	8.1	0
	6	134	55	55	45	**289**	0	90	0	8.1	0
	7	134	44	41	9	**228**	0	10	0.83	7.1	0
	8	143	48	48	14	**253**	0	90	0.83	7.1	0
	9	146	46	45	0	**237**	0	10	0	5.2	1
	10	146	49	47	0	**242**	0	90	0	5.2	1
	11	111	38	36	0	**185**	0	10	0.83	4.8	1
	12	130	43	41	0	**214**	0	90	0.83	4.8	1
	13	178	71	56	0	**305**	0	10	0	8.2	1
	14	177	63	53	0	**293**	0	90	0	8.2	1
	15	124	50	45	0	**219**	0	10	0.83	7.1	1
	16	152	55	49	0	**256**	0	90	0.83	7.1	1
	17	72	41	46	67	**225**	0	50	0.42	5.8	0
	18	144	50	48	0	**242**	0	50	0.42	5.9	1
2. Unbleached	7	129	51	47	14	**240**	0	10	0.83	8	0
	8	128	49	47	13	**238**	0	90	0.83	8	0
	15	137	51	42	0	**230**	0	10	0.83	8.2	1
	16	149	53	45	0	**247**	0	90	0.83	8.2	1
	17	81	39	41	51	**212**	0	50	0.42	6.5	0
	18	144	51	48	0	**244**	0	50	0.42	6.5	1
3. Unbleached	1	28.8	34.1	39.9	111.2	**214**	0	5	0	4.8	0
	2	31.5	36.2	44.7	123.6	**236**	0	90	0	4.8	0
	3	19.5	22.0	25.6	69.1	**136**	0	5	2	4.5	0
	4	23.9	28.0	34.4	94.3	**181**	0	90	2	4.5	0
	5	34.6	54.7	46.3	125.6	**261**	0	5	0	7.7	0
	6	34.9	49.8	52.9	145.5	**283**	0	90	0	7.7	0
	7	24.5	38.5	33.6	90.3	**187**	0	5	2	7.2	0
	8	28.1	35.7	41.9	114.5	**220**	0	90	2	7.2	0
	9	126.3	41.6	38.7	1.0	**208**	0	5	0	4.9	1
	10	157.0	50.5	48.4	0.2	**256**	0	90	0	4.9	1
	11	109.8	37.5	33.8	0.0	**181**	0	5	2	4.6	1
	12	128.9	42.0	38.1	0.1	**209**	0	90	2	4.6	1
	13	145.4	62.1	47.9	0.2	**256**	0	5	0	7.8	1
	14	171.6	61.1	57.4	0.3	**291**	0	90	0	7.8	1
	15	94.1	37.7	28.9	2.4	**163**	0	5	2	7.2	1
	16	138.7	47.6	41.5	1.8	**230**	0	90	2	7.2	1
	17	30.5	40.0	44.5	122.6	**238**	0	50	1	6.8	0
	18	168.2	56.9	51.1	0.0	**276**	0	50	1	6.9	1
1. Bleached	1	26	21	37	102	**185**	1	5	0	5.3	0
	2	29	23	41	118	**212**	1	90	0	5.3	0
	3	24	19	33	93	**170**	1	5	2	5.2	0
	4	29	21	40	114	**205**	1	90	2	5.2	0
	5	33	35	44	123	**236**	1	5	0	8.90	0
	6	35	35	51	145	**266**	1	90	0	8.90	0
	7	38	31	38	99	**206**	1	5	2	8.70	0
	8	48	32	49	117	**246**	1	90	2	8.70	0
	9	90	28	25	0	**142**	1	5	0	5.1	1
	10	108	32	31	0	**171**	1	90	0	5.1	1
	11	79	25	22	0	**127**	1	5	2	5.1	1
	12	103	33	29	0	**164**	1	90	2	5.1	1
	13	123	35	40	0	**198**	1	5	0	8.4	1
	14	149	37	49	0	**235**	1	90	0	8.4	1
	15	95	29	28	0	**153**	1	5	2	8.2	1
	16	125	32	34	0	**191**	1	90	2	8.2	1
	17	33	27	46	123	**230**	1	50	1	6.7	0
	18	111	31	36	0	**178**	1	50	1	6.4	1
2.Bleached	1	21.4	12.4	36.2	105.5	**176**	1	5	0	5.2	0
	3	19.3	12.8	32.7	95.8	**160**	1	5	2	5.1	0
	5	23.6	22.6	43.7	127.7	**218**	1	5	0	9.1	0
	7	20.4	17.2	41.2	118.1	**197**	1	5	2	9	0
	9	85.0	19.3	31.3	0.1	**136**	1	5	0	5.2	1
	11	72.8	15.3	30.4	0.0	**119**	1	5	2	5.1	1
	13	91.2	22.8	38.1	0.3	**152**	1	5	0	8.7	1
	15	68.7	18.8	29.4	0.2	**117**	1	5	2	8.5	1

Appendix 8

Multivariate experiment I; the wood resin analyses from the pulp samples.

Unbleached pulp, mg/g				
Sample	Unbl 1	Unbl 2		
Free fatty acids	1.34	1.45		
Resin acids	1.55	1.60		
Lignans	2.88	2.86		
Sterols	0.35	0.35		
Sterylesters	1.69	1.74		
Triglyserides	4.47	4.49		
Wood resin	9.41	9.63		
1. Bleached, mg/g				
Sample	Bleached	Lipase treated and bleached		
Free fatty acids	1.16	3.91		
Resin acids	0.71	0.83		
Lignans	0.70	0.37		
Sterols	0.19	0.19		
Sterylesters	1.39	1.26		
Triglyserides	3.39	0.02		
Wood resin	6.84	6.20		
2. Bleached, mg/g				
Sample	Bleached		Lipase treated and bleached	
Free fatty acids	0.83	0.82	3.61	3.64
Resin acids	0.63	0.63	0.79	0.78
Lignans	0.45	0.39	0.32	0.31
Sterols	0.21	0.18	0.17	0.18
Sterylesters	1.26	1.26	1.09	1.08
Triglyserides	3.60	3.55	0.06	0.03
Wood resin	6.53	6.43	5.72	5.72

Appendix 9

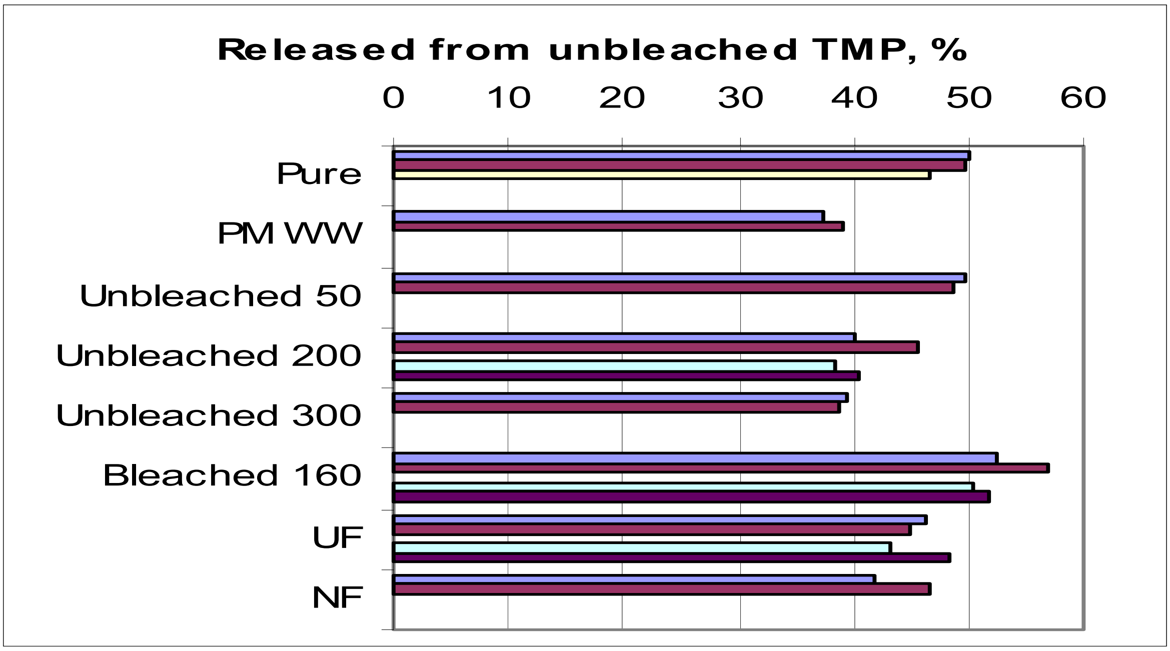
Multivariate experiment I; the retention results.

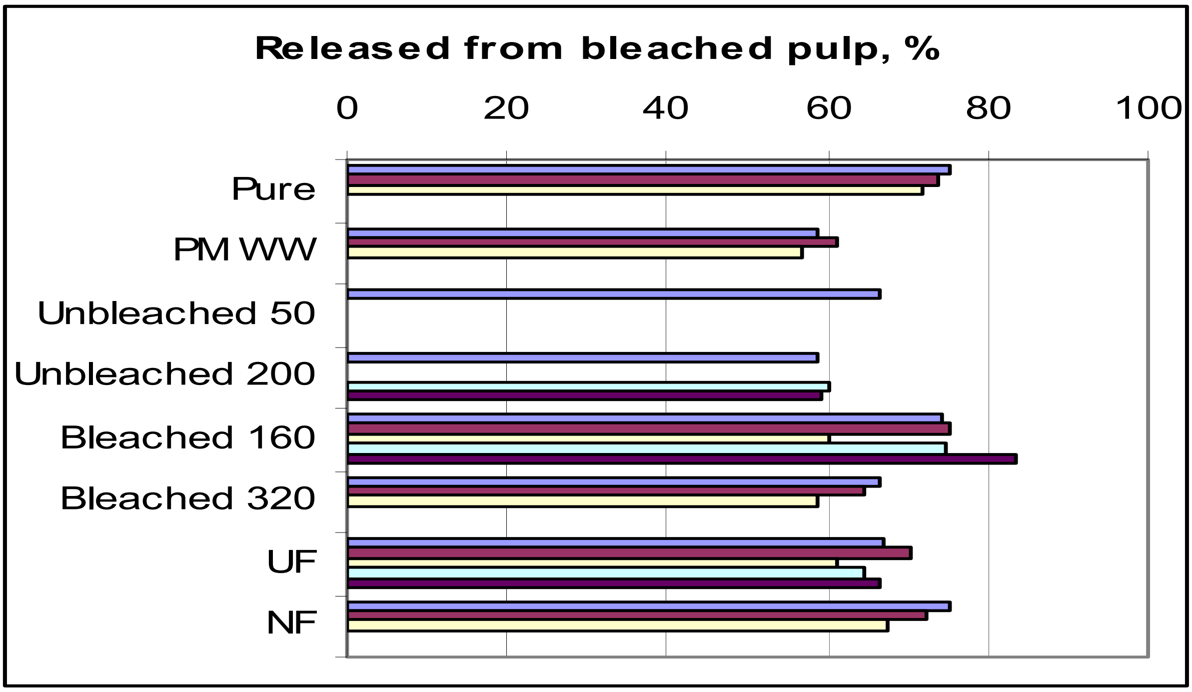
1. Unbleached	No.	Wood resin	FFA	RA	SE	Wood resin-RA
	1	51	54	50	49	51
	2	46		44	43	48
	3	58		54	54	59
	4	40		40	37	38
	5	36		14	45	41
	6	40		21	45	41
	7	39		10	35	46
	8	42		27	36	45
	9	50	53	46	44	51
	10	44	46	43	40	44
	11	36	38	33	33	37
	12	40	42	40	38	41
	13	44	47	31	49	48
	14	38	43	23	40	42
	15	42	45	36	41	44
	16	44	47	39	40	45
	17	45		44	42	46
	18	46	49	44	42	47
2. Bleached	1	61	63	27	64	63
	3	56	62	26	49	59
	5	46	20	-13	48	53
	7	52	39	6	50	56
	9	42	39	38	55	43
	11	44	43	21	57	47
	13	28	28	4	42	32
	15	43	43	19	57	47
	Retention in relation to the retention of wood resin-resin acids					
	No.	FFA	RA	SE		
1. Unbleached	1	1.07	0.99	0.96		
	2		0.92	0.89		
	3		0.91	0.91		
	4		1.05	0.97		
	5		0.33	1.09		
	6		0.52	1.10		
	7		0.23	0.76		
	8		0.61	0.81		
	9	1.04	0.91	0.86		
	10	1.03	0.97	0.90		
	11	1.03	0.88	0.90		
	12	1.02	0.98	0.93		
	13	0.99	0.66	1.04		
	14	1.02	0.55	0.95		
	15	1.02	0.83	0.94		
	16	1.04	0.87	0.89		
	17		0.96	0.91		
	18	1.04	0.94	0.89		
2. Bleached	1	0.99	0.43	1.02		
	3	1.05	0.44	0.84		
	5	0.38	-0.25	0.91		
	7	0.70	0.11	0.88		
	9	0.91	0.88	1.28		
	11	0.92	0.45	1.21		
	13	0.86	0.14	1.32		
	15	0.91	0.41	1.21		

Multivariate experiment II; the results.

								Level 0	5 min	Normal	5	no	25
								Level 1	20 min	Direct centrifugation	8	yes	60
LIGN	No.	FFA, mg/l	RA, mg/l	ST, mg/l	SE, mg/l	TG, mg/l	Wood resin, mg/l	Turbidity/ Wood resin	**Mixing, min**	**Dewatering method**	**pH**	**Lipase**	**Temperature, °C**
47	1	9	10	3	17	38	77	4.2	0	0	0	0	0
48	2	16	17	5	28	68	134	4.1	1	0	0	0	0
48	3	8	8	3	13	29	60	3.8	0	1	0	0	0
48	4	12	13	4	22	50	101	3.7	1	1	0	0	0
48	5	15	27	4	26	59	133	4.3	0	0	1.03	0	0
51	6	20	32	6	40	91	189	4.2	1	0	0.93	0	0
48	7	14	25	3	19	44	106	4.2	0	1	1.03	0	0
50	8	17	29	5	32	71	154	3.9	1	1	0.93	0	0
50	9	46	15	4	21	0	87	4.4	0	0	0	1	0
50	10	83	27	5	35	0	151	4.3	1	0	0	1	0
49	11	34	12	3	16	0	65	4.2	0	1	0	1	0
51	12	67	22	5	28	0	122	3.8	1	1	0	1	0
53	13	53	28	4	25	0	110	4.2	0	0	1.07	1	0
52	14	87	40	5	40	0	172	4.1	1	0	1	1	0
52	15	43	25	4	20	0	93	4.1	0	1	1.07	1	0
52	16	70	36	5	34	0	144	3.9	1	1	1	1	0
72	17	14	17	6	29	65	131	4.4	0	0	0	0	1
74	18	20	23	7	39	90	180	4.5	1	0	0	0	1
70	19	9	10	5	17	36	76	3.9	0	1	0	0	1
75	20	13	16	5	26	59	119	4.1	1	1	0	0	1
78	21	21	33	6	37	86	183	4.7	0	0	1.07	0	1
82	22	26	37	7	48	105	222	4.5	1	0	0.93	0	1
84	23	21	36	5	30	66	158	3.9	0	1	1.07	0	1
81	24	22	34	6	37	85	184	4.2	1	1	0.93	0	1
73	25	71	23	6	31	0	131	4.3	0	0	0	1	1
72	27	45	14	5	19	0	83	3.7	0	1	0	1	1
77	28	70	22	6	30	0	127	3.9	1	1	0	1	1
74	29	95	41	6	38	0	180	4.3	0	0	1.03	1	1
78	30	116	43	7	47	0	212	4.3	1	0	0.9	1	1
75	31	77	36	5	30	0	149	3.9	0	1	1.03	1	1
74	32	91	38	6	36	0	171	4.3	1	1	0.9	1	1

The quality of the dilution water; results at the parallel experiment points.





Appendix 12

The quality of the dilution water; the analyses carried out on the dilution water samples used in the experiment.

		Bleached 160	UF	NF	PM WW
pH		6.6	6.5	6.2	4.28
Conductivity	**µS/cm**	4300	4400	1100	1339
Turbidity	**NTU**	910	1	1	
Charge	**µekv/kg**	-3200	-510	-3	
non-volatile residue	**g/l**	7.8	5.8	1.2	
Ash content	**g/l**	3.6	3.4	0.6	
TOC	**mg/l**	2633	1750	245	275
lignin	**A 280 nm**	18	13	2	
Chloride	**mg/l**	47	53	16	
Sulphate	**mg/l**	590	551	5	
Mn	**mg/l**	7.43	6.95	0.02	0.39
Fe	**mg/l**	0.853	0.779	-0.075	
Na	**mg/l**	**1259**	**1180**	**135**	
K	**mg/l**	26	36	4	
Mg	**mg/l**	11	9	0	
Ca	**mg/l**	32	22	1	16
Si	**mg/l**	102	65	24	
Al	**mg/l**	1.33	0.77	0.00	3.07
Galactoglukomannaans	**mg/l**	**762**	**111**	**0.9**	
Pectines	**mg/l**	**323**	**85**	**3**	
Starch	**mg/l**	32	13	3	
Arabinose	**mg/l**	56	22	3	
Rhamnose	**mg/l**	13	4	0	
Xylose	**mg/l**	29	11	2	
Glukuronic acid	**mg/l**	31	6	1	
Galakturonic acid	**mg/l**	346	90	3	
Mannose	**mg/l**	594	86	0.7	
Galactose	**mg/l**	199	34	2	
Glucose	**mg/l**	184	36	3	
Total carbohydrates	**mg/l**	**1452**	**289**	**14.7**	
Lignans	**mg/l**	81	19	20	
Free fatty acids	**mg/l**	17.5	0.4	0	
Resin acids	**mg/l**	19.7	4.8	1.3	
Sterols	**mg/l**	7.0	0.2	0.2	
Sterylesters	**mg/l**	38.4	0.3	0.3	
Triglycerides	**mg/l**	79	0	0	
Wood resin	**mg/l**	161	6	2	

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