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Applicability of fractionation of softwood and hardwood kraft pulp and utilisation of the fractions

Sari Asikainen



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Sari Asikainen

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Preface

The experimental work included in this thesis has been carried out between 2000 and 2007. This thesis work was part of the following KCL projects Optimal reinforcement fibers, Improved birch fiber properties and Novel products from birch. The fractionation trials were done in co-operation with Noss AB (nowadays owned by Kadant Inc.).

In 2007 just when I was going to maternity leave my colleagues of the time, Agneta Fuhrmann and Leif Robertsén, put an idea of making a thesis into my head. However, it took some time before the writing work really started. Writing process of this work was done at VTT between 2010 and 2014. I would like to express my gratitude to VTT for giving me the opportunity to finalize the thesis.

I would like to show my gratitude to Agneta Fuhrmann, I sincerely appreciate her help, supportive words and positive attitude over the years. I thank Dr. Leif Robertsén for the encouragement and confidence boost in the final stage of the project.

I wish to thank my supervisor and custos Professor Olli Dahl for his interest in my work and that he patiently waited the accomplishment of the thesis.

I acknowledge Professor Ulf Gemgård and Professor Arnis Treimanis for reviewing the manuscript of my thesis and for their valuable suggestion.

I would like to thank all the co-authors of the original publications.

A lot of people from former KCL have contributed to the work and I am deeply indebted to them for their help. I am also thankful to my present colleagues at VTT.

I owe sincere thanks to my precious friend Päivi!

Most of all, I want to thank my family for their love and for always being there for me!

Espoo, December 7th, 2014

Sari Asikainen

Academic dissertation

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List of publications

This thesis is based on the following original publications which are referred to in the text as I–V. The publications are reproduced with kind permission from the publishers.

- I Asikainen, S., Fuhrmann, A., Robertsén, L. (2011) Effect of cell wall thickness and fines on bleaching of softwood kraft pulp, *Appita* 64:4, 362–367.
- II Asikainen, S., Fuhrmann, A., Ranua, M., Robertsén, L. (2010) Effect of birch kraft pulp primary fines on bleaching and sheet properties, *Biore-sources* 5:4, 2173–2183.
- III Asikainen, S. (2013) Reinforcing ability of fractionated softwood kraft pulp fibres, *Nord. Pulp Pap. Res. J.* 28:2, 290–296.
- IV Asikainen, S., Fuhrmann, A., Robertsén, L. (2010) Birch pulp fractions for fine paper and board, *Nord. Pulp Pap. Res. J.* 25:3, 269–276.
- V Asikainen, S., Fuhrmann, A., Kariniemi, M., Särkilähti, A. (2010) Evaluation of vessel picking tendency in printing, *O Papel* 71:7, 49–61.

Author's contributions

The author's role in each of the publications has been the following:

- I The author planned and supervised the experimental work and wrote the manuscript of the paper taking into account the comments of the co-authors.
- II The author planned and supervised the experimental work and wrote the manuscript of the paper taking into account the comments of the co-authors.
- III The author wrote the manuscript of the paper, and planned the experimental work.
- IV The author wrote the manuscript of the paper taking into account the comments of the co-authors, and planned the experimental work in co-operation with the co-authors. The author supervised the experimental work.
- V The author planned the experimental work and wrote the manuscript of the paper taking into account the comments of the co-authors.

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Publications I–V

Abstract

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List of symbols

P	Primary wall
S1	Outer layer of the secondary wall
S2	Middle layer of the secondary wall
S3	Inner layer of the secondary wall
M	Middle lamella
CWT	Cell wall thickness
PhOH	Phenolic hydroxyl groups
UB	Unbleached
C	Chlorine stage
D	Chlorine dioxide stage
E	Alkaline extraction stage
EO	Pressurized alkaline extraction stage
EOP	Hydrogen peroxide assisted pressurized alkaline extraction stage
H	Hypochlorite stage
Q	Chelation stage
P	Hydrogen peroxide stage
PO	Pressurized hydrogen peroxide stage
O	Oxygen delignification stage
O/O	Two stage oxygen delignification without intermediate washing
N	Neutralization stage
e	Neutralizing washing
Z	Ozone stage

EDTA	Ethylenediaminetetra acetic acid
DTPA	Diethylenetriaminepenta acetic acid
OXE	Oxidation equivalents
WRV	Water retention value
CSF	Canadian standard freeness
RRm	Mass reject rate
DDJ	Dynamic drainage jar
CTMP	Chemi-thermo mechanical pulp
TMP	Thermo mechanical pulp
GW	Ground wood
SRE	Specific refining energy
SEL	Specific edge load
rpm	Revolutions per minute
PC	Post colour number
RH	Relative humidity
ICP-AES	Inductively Coupled Plasma Atomic Emission spectroscopy
GC-FID	Gas chromatograph with flame ionization detector

1. Introduction

For a pulp mill producing 500,000 tons/year of chemical pulp, wood raw material accounts for over 50% (<http://www.wri-ltd.com/woodFiberIndex.cfm>) of all production-related costs. For market pulp, wood costs are over 40% (Kangas et al. 2013) of the mill net price of the product in Scandinavia. Thus, if this expensive fibre material is used as efficiently as possible, considerable savings in production costs are possible.

In theory, pulp mills can buy the optimal raw material for their products. In practice, the scope for influencing raw material selection is limited. Fractionation of the final or semi-finished fibres could thus be one way to optimize the use of fibres for specific paper and pulp grades. Furthermore, fractionation before bleaching can improve the selectivity of bleaching chemicals and prevent fibre damages caused by the bleaching chemicals during bleaching.

The idea of fractionation has been used for many years, but it has been largely limited to mechanical pulp and wastepaper (Karnis 1997, Williamson 1994, Wakelin and Corson 1997, Corson et al. 1996, Repo and Sundholm 1995, Ora et al. 1993). Driven by the need for strength improvement, refining energy savings, the development of new pulp and paper grades fractionation combined with refining has become a flexible tool to optimize the properties of chemical softwood pulp fibres (Sloane 2000, Vomhoff and Grundström 2003, Panula-Ontto 2003, Olson et al. 2001, Häggblom-Ahnger 1998, Koskenhely et al. 2005, Paavilainen 1993, El-Sharkawy et al. 2008a).

Fractionation of softwood kraft pulp has been widely studied (Sloane 2000, Vomhoff and Grundström 2003, Panula-Ontto 2003, Olson et al. 2001, Häggblom-Ahnger 1998, Koskenhely et al. 2005, Paavilainen 1993, El-Sharkawy et al. 2008a), but research on the reinforcing ability of different fibre fractions has not been published earlier. Applicability of fractionation to bleached eucalyptus pulp has been studied to some extent. In these studies the aim have been to improve sheet properties and to separate vessel elements (El Sharkawy et al. 2008b, Demuner 1999, Ohsawa et al. 1982, Ohsawa et al. 1984 Uchimoto et al. 1988). Fractionation of birch has not been extensively studied; properties of birch kraft pulp fractions with softwood kraft or mechanical pulp have not been published earlier.

1.1 Thesis objectives

The objectives of this thesis were to study the applicability of fractionation of softwood and hardwood kraft pulp and utilisation of the fractions. The research tasks for achieving this were:

- 1) To find out the reinforcing ability of the softwood kraft pulp fractions.
- 2) To elucidate the overall effectiveness of various bleaching chemicals on softwood kraft pulp fibres of different cell wall thickness.
- 3) To evaluate the applicability of fractionation before the bleaching, and the effect of birch and softwood kraft pulp primary fines on bleaching.
- 4) To clarify the effect of fractionation on chemical and physical properties of birch pulp and utilisation of the fractions in fine paper and board.
- 5) To evaluate the possibilities of utilising the birch fines fraction, unbleached or bleached, as a bonding agent for e.g. chemimechanical pulp.
- 6) To evaluate the applicability of fractionation of eucalyptus pulp, and the effects of eucalyptus kraft pulp vessel content, vessel size, vessel shape, and pulp refining on the vessel picking tendency.

Paper I and Paper II focused on the applicability of fractionation for unbleached pulp. Papers II, III and IV addressed the utilisation of the softwood and birch pulp fibre fractions for paper and board. Paper III and IV discussed the separate refining of the fibre fractions. In Paper III the softwood kraft pulp fibre fractions obtained by hydrocycloning were separately refined and the effect of the separate refining of the thin- and thick-walled fibre fractions on paper properties was discussed. In Paper IV the vessel rich fraction of the eucalyptus pulp was separately refined and the effect of that on vessel picking tendency was clarified. Structure of this thesis is shown in Table 1.

Table 1. Structure of this thesis.

Research question	Softwood	Hardwood
Applicability of fractionation before the bleaching	Paper I	Paper II
Applicability of fractionation after the bleaching – separate refining of the fibre fractions	Paper III	Paper V
Utilisation of the fibre fractions	Paper III	Paper II and IV

2. Softwood

The wood in softwoods is composed of two different cell types – tracheids (90–95%) and ray cells (5–10%). The tracheids in Scandinavian softwood are long and narrow with average length of 2–4 mm and an average width of 0.02–0.04 mm. The ray cells – parenchyma cells and ray tracheids – are 0.1–0.16 mm long and 0.002–0.050 mm wide (Rydholm 1965).

2.1 Softwood earlywood and latewood

In softwoods, the earlywood cells are formed at the beginning of the season when a growth hormone called auxin is plentifully available. Their primary function is to transport water. They have a large radial diameter, wide lumen, and thin cell walls. Latewood cells are formed at the end of the season when the supply of photosynthate is plentiful. Latewood gives mechanical strength to the stem. Latewood cells have a smaller radial diameter and have a small lumen and thick cell walls. Due to their differences in diameter, cell wall thickness, and coarseness, earlywood and latewood cells differ considerably in their papermaking properties (Hakkila 1998). Figure 1 shows structure of wood (http://www.wolman.de/en/infocenter_wood/from_tree_to_wood/wood_properties/aufbau_der_nadelhoelzer/index.php).

In pine (*Pinus sylvestris*) the latewood content variation is 15–50% (volume), and on the average 25%. In Norway spruce (*Picea abies*) the content of latewood is a little lower, averaging 15% (Jalava 1952).

The variation in latewood content depends on: heredity, habitat, growth rate, geographical location and location within stem. In general, the latewood content of very fast growing or very slow growing pine is lower, while pine growing at a moderate rate (7–8 annual rings/cm) has the highest latewood content (Jalava 1933). Pine from northern Finland and southern Finland have been found to have the following latewood contents:

- Northern Finland 17.5% (Siimes 1938)
- Southern Finland 21.9%
- Northern Finland 21.9% (Jalava 1933)
- Southern Finland 28.2%

The proportion of latewood changes with the height above ground, with the stump containing more latewood than the top. More latewood is needed in the stump to bear the weight and to resist the twist caused by the wind (Jalava 1933). Pine in northern and southern Finland form heavier wood up to the age of 50–60 years when the growing soil is moderate and the growing conditions are normal. After that the weight of wood formed is constant up to 100 years, after which it decreases. Sawmill chips contain mainly mature wood and its content of latewood is much higher than of earlywood (Jalava 1933).

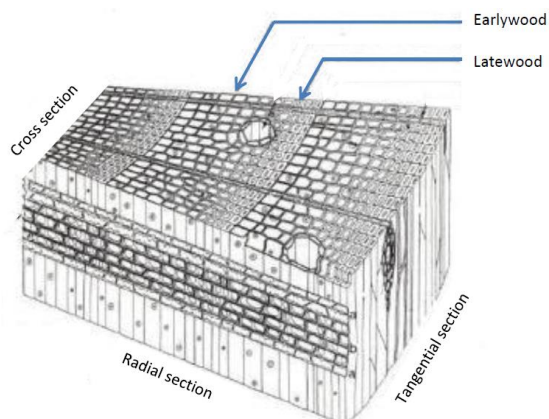


Figure 1. Structure of wood, modified from http://www.wolman.de/en/infocenter_wood/from_tree_to_wood/wood_properties/aufbau_der_nadelhoelzer/index.php.

2.2 Volumetric weight and cell wall density

Because of their thicker cell walls and small number of pores, latewood fibres have higher volumetric weight than earlywood fibres (Jalava 1952). The basic density of latewood in softwoods with thick-walled fibres is 2–3 times higher than that of earlywood, which, by definition, has thin-walled fibres. According to Spurr and Hsiung (1954), the basic density of latewood in softwoods is 600–900 kg/m³ and in earlywood 250–320 kg/m³.

Since the variation of wood density within a tree species depends on the variation in cell wall thickness in relation to the diameter of the lumen, wood density can predict and determine the properties of fibres and pulp (Hakkila 1998). Low-density wood absorbs water and chemicals more readily than dense wood in pulping. Mixed cooking of chip particles with wide density range therefore causes yield losses in chemical pulping, since low-density wood will overcook or high-density wood will undercook. High amounts of thick-walled, coarse fibres also lengthen the beating time requirement and make the sheet formation more difficult. Hakkila (1998) also claimed that because of their pale colour, thin-walled, earlywood fibres require less bleaching to reach a desirable degree of brightness.

The following cell wall density values and void volume values have been measured for latewood and earlywood fibres, Table 2 (Stone 1964, Gindl and Grabner 2000).

Table 2. Density of cell wall. (Douglas fir, western red cedar, pacific silver fir, Sitka spruce, western hemlock. Values similar for all species. Values are averages.) (Stone 1964, Gindl and Grabner 2000.)

	Density of cell wall g/cm ³	Void volume % of wall volume
Latewood	0.80, 0.81	48.3
Earlywood	0.30, 0.45	70.8

2.3 Fibre length

Earlywood and latewood fibres have roughly equal length. According to Sirviö and Kärenlampi (1998) the length of pulp fibres does not correlate with any other property measured from the fibres of the pulps. This finding supports the hypothesis according to which fibre length does not appreciably change during one growing season in *Pinus sylvestris*. It is obvious that the cross-sectional area of cell wall increases from earlywood to latewood, and if latewood fibres were considerably longer, a correlation should be found between the length and the cross-sectional area.

2.4 Fibre diameter

Earlywood fibre is wider than latewood fibre (Table 3). In the tangential direction the cell diameters of earlywood and latewood are almost the same. In the radial direction the earlywood tracheid is much wider than the latewood tracheid (Table 3, Fig. 1).

Table 3. Number of cells/mm², tangential diameter and radial cell diameter of spruce and pine earlywood and latewood (Johansson 1940).

	Number of cells/mm ²	
	Spruce	Pine
Earlywood	1060	1310
Latewood	1960	2050
Tangential diameter (µm)		
Earlywood	31.0	25.3
Latewood	28.8	23.5
Radial cell diameter (µm)		
Earlywood	30.3	30.2
Latewood	17.7	20.8

2.5 Cell wall thickness and proportion of cell wall layers

In the case of softwood there is a considerable difference in cell wall thickness between latewood and earlywood (Table 4) (Johansson 1940).

Table 4. Cell wall thickness of earlywood and latewood in spruce and pine (Johansson 1940).

	Cell wall thickness, μm	
	Spruce	Pine
Earlywood	1.54	1.54
Latewood	2.38	3.38

According to Jalava (1952) the cell wall thickness of pine and spruce earlywood is 2–4 μm and that of latewood is 2–3 times greater, i.e. 4–8 μm . Cell wall thickness varies along the stem from butt to top and also with age. Generally it can be said that the cell wall thickness of latewood depends on growing conditions. If conditions are very poor, the tree cannot grow cells with thick walls. Growing conditions can also be too good for the formation of cells with thick walls (Jalava 1952).

The proportions of the different cell wall layers vary in latewood and earlywood of spruce tracheids (Table 5) (Fengel 1969). The proportion and also the thickness of the S2 layer are higher in latewood. The proportions of P and S1 layers are higher in earlywood, but there is no difference in the thickness of the layers between earlywood and latewood.

Table 5. Proportions of different cell wall layer in spruce tracheids (Fengel 1969).

Layer	Earlywood		Latewood	
	Thickness μm	Proportion %	Thickness μm	Proportion %
P	0.1	6	0.1	2
S1	0.2	13	0.3	7
S2	1.4	79	4.0	90
S3	0.03	2	0.04	1
Total	1.7		4.4	

2.6 Strength and stiffness

Latewood fibres are about twice as strong per unit cross-sectional area as earlywood fibres. The morphological features of earlywood fibres, such as well-developed bordered pits, cross-field pits and greater number of pits, are the suspected reasons for the difference in strength. The relatively low proportion of the earlywood fibre wall composed of the middle layer of the secondary wall (S2 layer), in which the fibril orientation is more axial than in the other wall layers, also

has an influence on strength (Sirviö and Kärenlampi 1998, Leopold and McIntosh 1961, Ifju and Kennedy 1962).

According to Duncer and Nordmann (1965) earlywood fibres are damaged more easily both mechanically and chemically during cooking. The number of fractures is higher in earlywood than in latewood (Kibblewhite 1976). However, Johansson et al. (2001) have found that in pulp samples taken from the blow tank and after oxygen delignification, latewood fibres are more brittle than earlywood fibres.

According to Hattula and Niemi (1988) latewood fibres are twice as stiff as earlywood fibres. Paavilainen (1985) has found that fibre stiffness increases linearly with increasing latewood content. According to Mohlin (1975), however, there is no significant difference in the conformability between earlywood and latewood fibres in low-yield chemical pulp. At higher yields (mechanical pulp) earlywood fibres have a somewhat better conformability than those of the latewood.

2.7 Papermaking properties

Cell wall thickness, fibre length and fibre strength all influence paper strength (Dinwoodie 1965). Cell wall thickness is an important factor affecting tensile index, bursting area and fold number. This is because it influences both flexibility and bonding ability. It has been clearly shown that about 80% of the variation in hand-sheet tear, burst and apparent density is explained by the wall thickness–diameter ratio. The influence of pulp fibre length is small when compared with that of the above ratio (Paavilainen 1993, Kibblewhite 1982).

Thin-walled fibres from low-density wood collapse and become ribbon like. This increases fibre bonding and the formation of dense, nonporous, opaque sheets. Low-density wood results in higher tensile and burst strengths and folding endurance and produces a smoother and closer sheet of paper (Hakkila 1998). Earlywood fibre networks are far easier to calender to reference smoothness than latewood fibre networks (Retulainen et al. 1993).

For high tear strength, thick-walled cells and dense wood are desirable. The tear index increases linearly as latewood kraft pulp is added to TMP. The tear index also increases, although not linearly, as earlywood kraft pulp is added to TMP. The addition of latewood fibres does not improve tensile strength at all. Earlywood fibres have a greater effect on the development of tensile strength (Retulainen 1991).

In conclusion, the properties of sheets made from thin-walled and thick-walled fibres can be described as follows:

Thick-walled fibres	high bulk, loose structure, coarse surface, poor formation, high porosity, high tear strength, low tensile strength
Thin-walled fibres	low bulk, smooth surface, dense structure, good formation and low porosity, low tear strength, high tensile strength

2.8 Chemical composition

The differences in chemical composition between latewood and earlywood are due to differences in the distribution of components in the cell wall. Latewood has a lower content of lignin due, indirectly, to the difference in cell wall thickness. At the beginning of the cell wall thickening process, the first 4–6 lamellae of the secondary wall form a 0.1–0.2 μm thick lignin-rich S1 layer (Hakkila 1998). In temperate softwoods, the S2 layer of the secondary wall varies widely in thickness. In latewood walls, it consists of approximately 30–40 lamellae and contains more cellulose and less lignin than the P and S1 layers. In earlywood walls, the S2 layer is considerably thinner. This is why the content of lignin is higher in thin-walled earlywood cells than thick-walled latewood cells (Hakkila 1998). The compound middle lamella (M+P) contains up to 0.88 g/g lignin, whereas the lignin content of the secondary cell wall of conifer tracheids ranges from 0.22 to 0.25 g/g (Fengel and Wegener 1989). Wilson and Wellwood (1965) found that earlywood was 2–3% richer in lignin than latewood. Table 6 shows the proportion and distribution of cellulose and lignin in earlywood and latewood of softwood (Fengel 1970).

Table 6. Proportion and distribution of cellulose and lignin in earlywood and latewood of softwood (Fengel 1970).

Layer	Cellulose, % of total cellulose		Lignin, % of total lignin	
	Earlywood	Latewood	Earlywood	Latewood
M+P	4	3	27	18
S1	9	5	10	8
S2+S3	87	92	63	74

Despite the higher lignin content and higher kappa number associated with earlywood, these pulps consistently gave higher brightness and lower colour reversion than latewood-derived pulp, suggesting that residual lignin is more accessible to bleaching reagents in the thin-walled fibres (Hergert et al. 1982).

Latewood contains more glucomannan and less glucuronoarabinoxylan (percentage) than earlywood, because earlywood has less S2 layer and more S3 layer. Table 7 presents the percentages of polysaccharides in pine earlywood and latewood (Meier and Wilkie 1959).

Table 7. Percentages of polysaccharides in earlywood and latewood of pine (Meier and Wilkie 1959).

	Earlywood		Latewood	
Galactan	6.8	3.4	4.3	3.1
Cellulose	54.8	56.7	55.5	56.2
Glucomannan	19.6	20.3	24.8	24.8
Arabinan	1.8	1.0	1.3	1.8
Glucuronoarabinoxylan	17.0	18.0	14.1	14.1

3. Hardwood

Hardwoods contain several types of specialized cells in widely varying proportions and for different functions. The four major cell types occurring in hardwoods are libriform fibres (supporting tissue), vessel elements (conducting tissue), parenchyma cells (storage tissue), and hybrids of these cell types classified as tracheids. The term fibre denotes specifically libriform fibres and tracheids. Libriform fibres of hardwood are shorter than softwood tracheids, averaging 1.1–1.2 mm in length and 0.014–0.040 mm in width (Rydholm 1965).

The proportion of vessels, fibres, and parenchyma cells vary with the species, Table 8 (Ilvessalo-Pfäffli 1995).

Table 8. Proportion of cells in hardwood (Ilvessalo-Pfäffli 1995).



Percent of total volume	<i>Betula verrucosa</i>	<i>Eucalyptus globulus</i>
Fibres	64.8	49.0
Vessels	24.7	21.0
Rays	8.5	14.0
Longitudinal parenchyma	2.0	16.0

3.1 Fibres

The primary function of fibres is to support the structure of the tree, although they can also conduct water. The fibres are therefore long, tapered narrow cells with closed ends and very thick walls. Fibres contribute 30–75% of the wood volume. Usually both libriform fibre and fibre tracheids are present in the same species. In birch fibres occupy about 65% of the wood volume (Table 8) (Ilvessalo-Pfäffli 1995, Hakkila 1998).

Compared to softwoods, hardwood fibres have a narrow fibre length distribution. Fibre length varies between 0.7 and 1.7 mm. Cell wall thickness varies from 2.5 μm to 5 μm , and fibre width from 15 to 40 μm (Ilvessalo-Pfäffli 1995). Narrow hardwood fibres, such as the eucalyptus fibres (e.g. *Eucalyptus globulus*, *Eucalyptus grandis*) used in papermaking can be quite thick-walled. The cell wall thickness of birch is comparable to that of eucalyptus fibres, but birch fibres are much wider (Table 9) (Paavilainen 2002, Hicks and Clark 2001).

Table 9. Fibre dimensions of birch and eucalyptus (Paavilainen 2002, Hicks and Clark 2001).

	Birch	Eucalyptus
		
Fibre length (av.), mm	0.9	0.7
Fibre width, μm	20	16
CWT, μm	4	4
Coarseness, mg/m	0.113	0.062
No. of fibres/g of pulp, million	8	13

3.2 Hardwood vessel elements

3.2.1 Dimensions of vessel elements

The vessels are composed of single cells; their size and distribution within the growth ring vary with species. Temperate zone hardwoods can be divided into three groups: diffuse-porous, ring-porous and semi-ring-porous. In diffuse-porous woods the vessels are fairly uniform in size and quite evenly distributed throughout the ring (e.g. *Betula*, *Populus tremula*). In ring-porous woods the earlywood vessel are much larger than those formed later in the season. In semi-ring-porous wood the vessels of earlywood are somewhat larger and more abundant than those of latewood (e.g. *Populus tremuloides*). The diffuse-porous is the most common among the papermaking hardwoods (Ilvessalo-Pfäffli 1995).

The proportion of vessels in most hardwoods is 10–40% of the volume. The proportion of vessels in birch is 25% of the volume, but less, about 4% of the mass. In most commercial eucalyptus species and clones the proportion of vessels in the wood volume ranges from 10 to 20% (Foelkel 2007). The vessel elements are shorter than hardwood fibres. The diameter of vessels varies greatly from species to species. For example in birch vessel elements are medium-long to long (up to 1.0 mm), and quite narrow compared for example to vessel elements of eucalyptus (Fig. 2), which can have vessel elements of width up to about 400 μm (Paavilainen 2002).

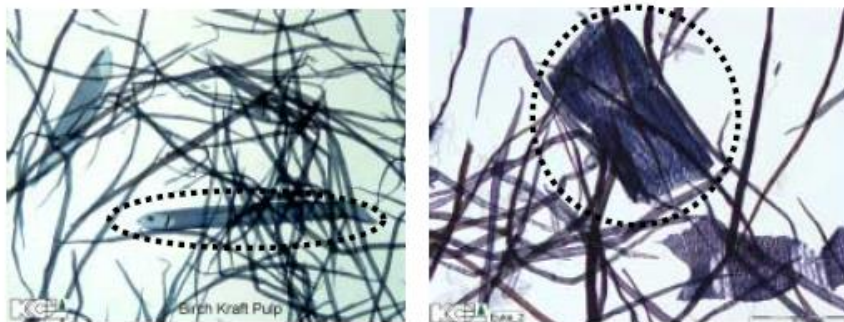


Figure 2. Vessel elements of birch (left) and eucalyptus (right).

The vessel wall is relatively thin, practically equal to the fibre wall thickness, between 2.5 and 5 μm .

3.2.2 Chemical composition of vessel elements

The chemical composition of the vessels is similar in its chemical constituents, but there are some difference between fibres and vessels. Vessel elements have been found to be richer in cellulose compared with fibres and lignin has been found in the vessel elements even after bleaching (Fardim and Lindström 2009). There are also indications that the lignin in vessels is more hydrophobic, richer in guaiacyl units than in syringyl (Watanabe et al. 2004). The syringyl to guaiacyl ratio may reach about 0.5 to 1 for the vessels, while that of the fibres is from 2 to 6 (Foelkel 2007). It has been also revealed that the xylan content of vessel elements is higher than that of the fibres (Figueiredo Alves et al. 2009).

3.2.3 Vessel picking

The composition of pulp elements influences interacting paper properties like strength and bonding (runnability), surface roughness and surface strength (printability). Papermaking properties of vessel elements are inferior, since they do not bond well and contribute little to the strength of paper. The vessel picking is common problem in printing papers containing hardwood pulps. The vessel picking trouble is a phenomenon that some of the hardwood vessel elements in the paper surface tend to be picked off by an ink-tackiness of the printing press (Ohsawa 1988). Hardwood vessel picking in the offset printing of uncoated fine papers is characterized by the appearance of small, white spots in solid and halftone areas in the print. These defects will repeat exactly in the same area of the print for several hundred impressions, but they will eventually become smaller and less intense until they fade away. The shapes of these white spots are either elongated or they may appear more as squares of the order of 1 mm or less in dimension. Vessels on the blanket of a conventional offset press are intrinsically oleophobic

because of preferential wetting by the fountain solution. These vessels become oleophilic and accept ink only after printing few hundred impressions. Thus, if a vessel picking problem is going to occur, it usually becomes evident after printing a few hundred sheets (Shallhorn and Heintze 1997).

It is generally known that vessel picking tendency is mainly caused by the presence of large vessel elements in hardwood pulps and the problem becomes more severe when the bonding strength between vessel elements and fibres is too weak (Ohsawa 1988). The number of vessel elements, which will be picked off during printing, is considered to be caused by the following factors, such as, 1) number, size and shape of the vessel elements in the paper surface, 2) bonding strength between vessel elements and paper sheet, and 3) number and bonding strength of fibres, which are covering vessel elements (Ohsawa 1988, Colley 1975).

Reduction of vessel picking tendency of hardwood pulps can be achieved by: 1) Reducing vessel content in a stock by selecting a suitable hardwood raw material, which has small and slender vessel elements and conformable fibres (Ohsawa 1987) or removing large and square-shaped vessel elements by using hydrocyclones (Ohsawa et al. 1982, Mukoyoshi and Ohsawa 1986, Mukoyoshi et al. 1986, Ohtake et al. 1987, Ohtake and Okagawa 1988); 2) Reducing size of the vessel elements by refining the pulp at high consistency (Ohsawa et al. 1984, Nanko et al. 1988) or refining the pulp with low refining intensity, i.e. low specific edge load (de Almeida et al. 2006, Joy et al. 2004); 3) Increasing vessel-to fibre bonding strength by increasing the conformability of fibres, by using pulp with high hemicellulose content, by surface sizing, by refining the pulp at high consistency (Ohsawa et al. 1984, Mukoyoshi et al. 1986) or by treating the pulp with carboxymethyl cellulose (Blomstedt et al. 2008, Rakkolainen et al. 2009); 4) Forming a suitable sheet structure, i.e. covering the vessel elements with fibres (Nanko et al. 1988); 5) Vessel picking can also be reduced by treating the pulp with enzymes (Uchimoto et al. 1988). Besides these pre-treatments paper manufacturing technologies (headboxes, papermachine, wet pressing, calendering) and printing machine characteristics (speed, temperature, fountain solution, ink supply, ink type and equipment cleanliness) affect the vessel picking.

3.3 Ray cells – primary fines

For papermaking materials fines are regarded as particles that pass through a 76 µm-diameter round hole or a 200-mesh screen of a fibre length classifier (Seth 2003).

Primary fines consist of ray cells, some broken fibres and thin sheets from the fibre surface. Primary fines usually represent between 1 and 3 percent of the o.d. pulp depending on wood species. Secondary fines are formed in refining. They come mostly from the fibre surface and have higher lignin content compared to the fibres, but lower compared to the primary fines (Lindström and Nordmark 1978, Htun and de Ruvo 1978). The fines fraction differs from the fibre fraction in that it has higher contents of lignin, metal ions (Table 10) and extractives (Bäckström

and Brännvall 1999, Liitiä et al. 2001, Hinck and Wallendahl 1999, Treimanis et al. 2009, Treimanis 2009). Fines have also been found to contain slightly more xylan and glucomannan. The lignin in primary fines has a high molar mass and few phenolic hydroxyl groups. The lignin in ray cells, the main constituent of primary fines, has shown more “condensed” lignin, with more aromatic carbon-carbon linkages than in other pulp fractions. The fines also had higher contents of carbon-yl groups (Bäckström and Brännvall 1999, Liitiä et al. 2001, Hinck and Wallendahl 1999).

Table 10. Lignin and metals contents of pulp and ray cells (unbleached softwood kraft pulp) (Heijnesson-Hulten et al. 1997).

	Lignin %	Mn mg/kg	Fe mg/kg	Cu mg/kg	Mg mg/kg	Ca mg/kg
Pulp	3.8	100	12	1.2	270	2631
Ray cells	8.1	178	146	25	587	1771

The primary fines from unbleached kraft pulp had a specific surface area of 25 m²/g, while the secondary fines (obtained after 25 minutes beating) had a surface area of 140 m²/g (Janes 1990). Permeability measurements have shown fines to have surface areas ranging from 10 to 50 m²/g, while the fibre fraction has surface areas of around 1 m²/g (Retulainen et al. 1993). The fines present in chemical pulp have a WRV two to three times that of the respective fibre fraction, while the content of inaccessible water is 5–7 times greater (Retulainen et al. 1993).

3.3.1 Extractives of birch pulp primary fine

The hardwood resin is located in the ray parenchyma cells, which are connected with the vessels. The resin consists of fats, waxes, and sterols. The accessibility of the resin depends on the pore dimensions as well as on the mechanical stability of the ray parenchyma cells. For instance, the accessibility of the resin in birch is much lower than that of the aspen (Sjöström 1981).

In birch the majority of the extractives are located inside the parenchyma cells. Birch pulp extractives cause severe problems in pulp and papermaking. Of the birch extractives, betulinol is usually the main component in precipitations or stickies found at both pulp and paper mills. Its melting point is 261°C, thus it is crystalline through the all stages of the pulp making. Sitosterol can be oxidized that results in a bad smell; sitostanol is again saturated and stable. Both are found in stickies although they are not sticky themselves (Back and Allen 2000). Fatty acids are sticky, especially saturated fatty acids in the form of metal soaps, and they have been found to impair the degree of sizing (Lidén and Tollander 2004). Both the fatty acids and sitosterol parts are oxidized, which can result in taste and odour problems. Especially, the unsaturated fatty acids are easily oxidized leading to volatile bad smelling aldehydes, such as hexanal and nonal (Oyaas 2002). All

lipophilic substances, which are enriched on the fibre surfaces, are decreasing the fibre-fibre bonding ability (Kokkonen et al. 2002).

Less birch extractives are removed during cooking than for example pine extractives for a number of reasons (Laamanen 1984):

- Most of the birch extractives are located inside the small ray cells, which have very small pore size.
- The composition of birch extractives makes them hard to remove by the pulping liquor. Birch does not contain free resin acids, which form resin acid soaps in alkaline pulping, and carry the remaining pitch into the pulping liquor. Birch contains high amounts of neutral extractives, and the fatty acid soap content produced from birch extractives during cooking is insufficient to transport these into the cooking liquor.
- Birch outer bark contains large quantities of a crystalline substance, betulinol. The debarking of birch at the mill is never complete, and thus varying amounts of betulinol find their way into the digester. Betulinol crystals are carried along with the pulp and appear in the final bleached product. Betulinol is a hydrophobic substance and bonds a part of the soaps formed from birch extractives during pulping, thus making the removal of the other neutral extractives more difficult.

3.3.2 Birch extractives in bleaching

The crystalline birch outer bark extractives (betulinol) are virtually inert during bleaching, while the extractives present in the ray cells contain some highly reactive components. In actual bleaching, however, the bleaching chemicals are not capable to penetrate into the extractives. They react only with the surface of the extractives. Laboratory experiments showed that the effect of the chemicals can be increased by increasing the surface area of the extractives (Laamanen 1984).

Unsaturated resin components can in principle react with oxygen, producing a complex mixture of oxidized products (Back and Allen 2000). In a laboratory study it was found that oxygen as employed in birch pulp bleaching is not able to penetrate into lipophilic resin aggregates. The composition of pulp resin was roughly the same before and after oxygen bleaching (Laamanen 1984).

Chlorine dioxide can also react with unsaturated resin components (Back and Allen 2000). Chlorine dioxide undergoes only heterogeneous surface reactions with resin particles and the reactions are slow (Laamanen 1984).

Like oxygen, hydrogen peroxide does not penetrate resin aggregate, and reactions occur essentially only with dissolved components (Back and Allen 2000). Hydrogen peroxide treatment of birch kraft pulp in the laboratory, with a large dosage of 5%, did not change the composition of the extractives (Laamanen 1984).

In laboratory experiments, it was found that ozone caused a considerable decrease in the resin content of birch kraft pulp. The effect was assumed to be main-

ly due to fairly vigorous mixing in the ozone treatment. It was concluded that ozone causes a marked surface oxidation (Laamanen 1984).

Alkaline extraction with washing efficiently removes chlorinated and oxidized resin. Chlorinated resin components are partly dechlorinated, and this will contribute to the hydrophilization of the resin, and thus promote subsequent deresination. Alkaline treatment also dissolves residual fatty and resin acids as sodium soaps, which then can act as dispersing and solubilizing agents and promote pulp deresination (Laamanen 1984).

The flows and distribution of extractives in two bleaching plants were clarified in the Nordic project – Keys to closing the bleaching loops (Fuhrmann et al. 2000). The results showed that the extractives content decreased substantially in the first alkaline hydrogen peroxide stages (OPP, PP) due to the ionization of fatty acids and micelle forming (Fig. 3) (Bergelin and Holmbom 2000). The results also showed that the betulinol is difficult to remove from the birch pulp in the bleaching.

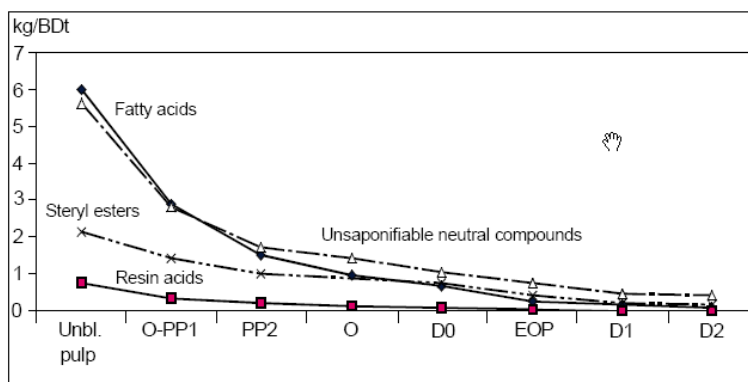


Figure 3. Deresination at a birch ECF kraft mill (Bergelin and Holmbom 2000).

4. Fractionation

Fractionation means separation of fibres into two or more fractions with different properties. The two basic types of industrial fractionation equipment are screens and hydrocyclones (Fig. 4a and b). Generally, screens fractionate according to fibre size and hydrocyclones according to the specific surface area of the fibre.

In the screening, particle acceptance is determined by fibre flexibility, length, and thickness in that order. Fibres of equal length are accepted by flexibility. Chemical fibres are more readily acceptable than stiff mechanical fibres. Fibres of different length are accepted by length, and shorter fibres are accepted more readily than long fibres. Shives (as long as fibres) are rejected because of their greater stiffness. Particle width or thickness is also a factor influencing particles of the same length, though the effect is not as strong as that of flexibility (Gullichsen 1999, Shallhorn and Karnis 1981, Karnis 1982, Saint Amand and Perrin 2000). Some separation on the basis of fibre coarseness can be obtained with very narrow slots (Karnis 1997, Saint Amand and Perrin 2000). The specific hydraulic surface area of fibres is a factor in screening. Fluid drag through the screen aperture causes fibres of greater specific surface area to be accepted more readily. Gravitational forces from tangential motion cause particles in the suspension to separate so that smaller and lighter particles accumulate toward the rotational centre. Screen rotors need to be designed to compensate for this unwanted fractionation (Gullichsen 1999).

In hydrocyclones, the separation of fibres is a result of the interplay between two forces, i.e. the centrifugal force moving fibres outward, and the hydrodynamic drag causing the fibres to move inward. The centrifugal force outward derives from the effective mass of the fibre suspended in water. The hydrodynamic force inward is a function of the surface area of the fibre. Experimental studies have shown that hydrocyclones separate fibres according to the specific surface area, specific volume and cell wall thickness (Karnis 1997, Saint Amand and Perrin 2000).

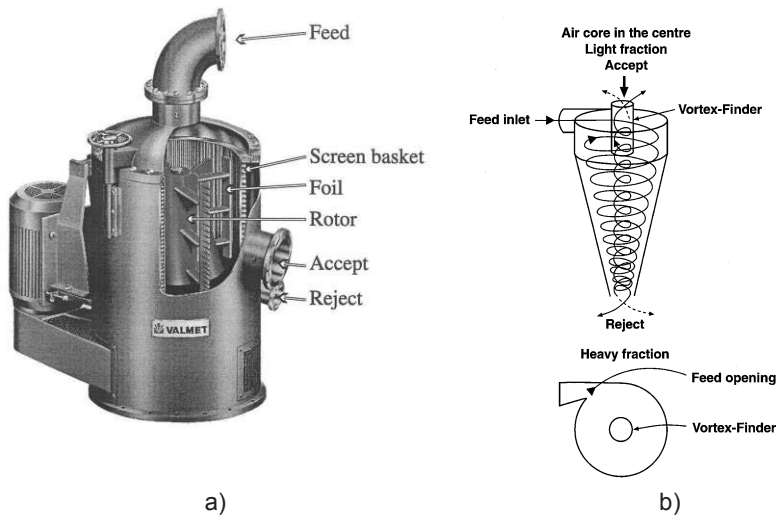


Figure 4. Valmet TAP pressure screen a), design of a typical hydrocyclone b) (Hautala et al. 1999).

According to Moller et al. (1999) fibre fractionation could be applicable (Fig. 5): 1) In the production of stratified paper or board, placing the different fractions where their particular properties are most needed in the sheet. 2) In selective paper making by fractionating a single fibre resource to suit different products being run simultaneously on different machines, or suit to individual machine characteristics. 3) In selective beating by splitting a pulp stream into two or more fractions, each of which is then beaten separately (or not at all) until optimum conditions are reached, and finally recombining the fractions.

To chemical pulp producers, fibre fractionation could also mean removing the fines fraction. In this way the remaining long fibre fraction could be refined to high-tensile strength at a given freeness (Allison and Olson 2000).

Fractionation should be carried out in higher consistencies than today to make it economically viable process. The normal range of fibre consistency in hydrocyclones is 0.3–0.9% (Jokinen 2007). Above this limit, fractionation is ineffective due to fibre flocculation. Studies have been made to develop hydrocyclones, which could be operated in higher consistency range (Levin and Vomhoff 2008). According to Borschke et al. (1998) fractionation with screens at low consistencies of about 1.0% provides advantages over fractionation at medium consistencies. At low consistencies, narrower slot widths may be used, and thus the screening and fractionation efficiency can be significantly improved. The disadvantage is that larger machines are required. According to Gullichsen et al. (1985) medium consistency (8–15%) is as efficient as low consistency screening.

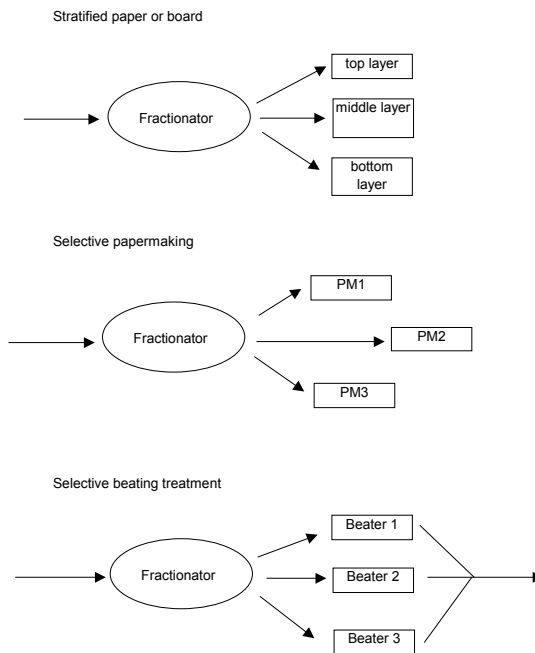


Figure 5. Fibre fractionation has many applications (Moller 1999).

4.1 Previous studies on fractionation of softwood pulp

Pesch (1963) discovered that latewood fibres settled out of slurry nearly three times as fast as earlywood fibres. From this difference in sedimentation rate, he conceived the idea that earlywood pulp could be separated from latewood in a centrifugal cleaner or hydrocyclone. He was granted a patent on this process in 1963. Pesch (1963) found that pulp from the cleaner accepts portion had better tensile properties and greater density. Pulp from the cleaner rejects portion had greater bulk, porosity, and tear. The best differentiation of properties was obtained when the feed pulp was diluted to 0.1–0.2% consistency before separation (Pesch 1963).

In 1966, Jones et al. (1966) reported that a process had been developed for separating bleached pine pulp into earlywood and latewood fractions using centrifugal cleaners. A single stage separation of southern pine pulp gave fractions containing about 70% of the desired fibres, depending on the cleaner operating conditions and pulp properties. The earlywood fraction formed a dense relatively non-porous sheet having higher Mullen (bursting strength), lower tear, and better smoothness than the original pulp. The latewood fraction formed a bulky, porous sheet with good formation, lower Mullen strength, and higher tear.

Alho (1966) studied the separation of unbleached softwood kraft pulp with hydrocyclones into four different fibre fractions with various coarseness values:

0.128 mg/m, 0.145 mg/m, 0.144 mg/m and 0.195 mg/m. The fibre fractions of coarseness 0.128 mg/m and 0.195 mg/m were bleached separately using the sequence C-N-H-E-D-E-D (C-chlorine, N-neutralization, H-hypochlorite, E-alkaline extraction, D-chlorine dioxide). No major difference was found in total chlorine consumption. The fraction 0.128 mg/m consumed 94.2 kg chlorine and the fraction 0.195 mg/m consumed 96.9 kg chlorine. The pulp with low coarseness had better tensile and burst strength. The pulp with high coarseness had higher tear strength, bulk, porosity and brightness.

In 1970, Olgård (1970) described the fractionation of fibre suspensions (softwood kraft pulp and birch pulp) by liquid column flow. When this system was applied to chemical pulps, the coarse fractions showed better strength than the original pulp, whereas finer fractions showed properties as good as those of the surface material.

Paavilainen (1992) studied the possibility of fractionating unbleached and bleached softwood sulphate pulps according to cell wall thickness. Three different fractionation methods, namely hydrocyclone, Johnsson fractionator and Jaquelin apparatus, were compared. The hydrocyclone gave the best separation efficiency. The hydrocyclone concentrated the thick-walled fibres in the reject fraction and thin-walled fibres in the accept fraction. The separation efficiency could be controlled by means of the accept to reject ratio. With a three-stage treatment the latewood content of the original pulp (20%) was increased up to 74% in the reject fraction, and reduced to 6% in the accept fraction with a single-stage treatment. In the hydrocyclone trial the stock concentration was 0.10% and temperature 7°C. Fines were removed before fractionation. The accept pulp had higher tensile strength than the reject pulp. The reject pulps gave a more porous sheet with higher tear strength. Karnis (1997) studied the separation of pulp fibres in various fractionating devices. It was shown that mechanical barrier fractionators (conventional screens) separated fibres according to length and flexibility, irrespective of the type of pulp used. Hydrodynamic separators behaved differently. The liquid plug fractionator separated fibres according to their length, the atomizer according to their diameter, and the hydrocyclone according to specific surface area and density.

Mansfield et al. (Mansfield and Saddler 1999, Mansfield et al. 1999) performed experiments with enzymes with the aim of improving the strength properties of bleached Douglas fir kraft pulp. Industrial-scale pressure screen fractionation was combined with a cellulase treatment of the long fibre fraction. Density and smoothness were improved in handsheets derived from the unrefined pulps. Both tensile index and burst index were increased by about 15% over the corresponding controls. However, the intrinsic fibre strength and tear strength were lower. According to these workers this technology offers several benefits, one being an improvement in sheet smoothness, which in turn improves paper printability. The treatment also reduced the refining energy required to attain in-plane paper strength, such as tensile strength. Furthermore, integration of an enzymatic treatment stage with refining provided a means of incorporating coarse feed stocks such as Douglas fir into the manufacture of some fine paper products.

El-Sharkawy et al. (2008a) used pressure screen fractionation as a tool to fractionate the softwood kraft pulp. Low intensity refining of the reject fraction was beneficial in preserving the average fibre length and in maintaining a higher tear index, but the expense of a higher energy input to reach a certain tensile index. The accept fraction of softwood kraft pulp was used to enhance the strength properties of once dried softwood pulp, reducing the refining energy input needed to reach a certain tensile index.

Removing primary fines from the softwood kraft pulp has been shown to lower the amount of active chlorine needed to reach a given brightness in a (C90+D10)EHDED bleaching sequence (Westermarck and Capretti 1988). Non-chlorine bleaching agents are sensitive to the presence of metal ions and it has been shown that removal of primary fines from softwood kraft pulp reduces the hydrogen peroxide consumption in a Q(EOP)QP(O) sequence, although it had only a limited effect on kappa number and pulp brightness (Heijnesson-Hulten et al. 1997). Removing primary fines from softwood kraft pulp before bleaching may facilitate water cycle closure of the bleaching by lowering the metal ion content (Bäckström and Brännvall 1999).

4.2 Previous studies on fractionation of hardwood pulp

Applicability of fractionation to bleached eucalyptus kraft pulp has been studied to some extent. A study performed by Demuner (1999) focused on the different responses of three fractionation technologies (hydrocyclone, pressure screen and “Spraydisc”) of an eucalyptus market pulp. The results showed that although eucalyptus has a narrow fibre length distribution, it was possible to separate two fractions (fines fraction and coarse fraction) from the pulp with different sheet properties. The most significant changes of the fibre characteristics (morphology and surface chemistry), and sheet properties were introduced by the hydrocyclone fractionation. The fines fraction had a higher fines content and also higher number of fibres per gram of pulp. Also the pentosans content and carboxyl content of the fines fraction was slightly higher. The fines fraction produced a sheet with lower porosity and bulk than the original pulp or the coarse fraction. The light scattering and smoothness of the fines fraction sheet was the highest.

El Sharkawy et al. (2008b) studied the fractionation of eucalyptus kraft pulp with pressure screens equipped with holed and slotted screens, and separate refining of the obtained fractions. The fractionation produced two different fractions with different fibre and sheet properties. He found that low intensity refining was beneficial for the reject fraction in preserving the tear index at a certain tensile index.

Ohsawa et al. (1982) found that it is possible to separate vessel elements from tropical hardwood pulps by hydrocyclone fractionation to the reject fraction, and in this way prevent vessel picking. After the vessel separation, the vessel enriched reject fraction can be beaten at high consistency (Ohsawa et al. 1984, or for example treated with enzymes (Uchimoto et al. 1988) to reduce the vessel picking problem.

5. Experimental

5.1 Raw materials

5.1.1 Softwood kraft pulps

Unbleached softwood kraft pulp from a Finnish mill (66% pine, *Pinus sylvestris* and 34% Norway spruce, *Picea abies*) was used in Paper I.

The bleached softwood kraft pulp used in Paper III was obtained from the UPM-Kymmene's Kaukas pulp mill. The pulp was produced using a Super Batch cooking system and O/O(EO)D(PO)D bleaching. According to the fibre furnish analysis the kraft pulp contained approximately 66% pine (*Pinus sylvestris*) and 34% spruce (*Picea abies*). About 50% of the raw material used at the mill was sawmill chips, and 50% had been chipped on site.

The pine pulp used in Paper IV was obtained from a Finnish mill.

5.1.2 Birch kraft pulps

An oxygen-delignified birch kraft pulp for the trials in Paper II and bleached birch kraft pulp for the trials in Paper IV were obtained from a Finnish mill.

5.1.3 Eucalyptus pulps

The bleached mill eucalyptus kraft pulps used in the trials in Paper V were *Eucalyptus globulus* from Southern Europe and *Eucalyptus grandis* from South America. Both pulps were mill-dried.

5.1.4 Mechanical pulps

Mechanical pulps (TMP, GW) for Paper III were obtained from UPM-Kymmene's Rauma mill. The properties of the mechanical pulps are shown in Table 11.

Table 11. Properties of the mechanical pulps.

	TMP	GW
CSF, ml	24	48
Length weighted av. fibre length, mm	1.16	0.82
Apparent bulk-density, kg/m ³	524	487
Tensile index, Nm/g	57.0	37.4
Tear index, mNm ² /g	6.93	3.78
Opacity, %	94.4	94.5
Light scatt. coeff., m ² /kg	70.0	74.0
Brightness, %	60.7	68.0
Scott bond, J/m ²	353	330

Unbleached softwood CTMP from a Finnish mill and TMP from KCL pilot plant were used in the experiments in Paper II.

5.2 Fractionation

5.2.1 Effect of cell wall thickness and fines on bleaching of softwood kraft pulp, Paper I

Unbleached softwood kraft pulp was fractionated using hydrocyclones in order to obtain pulps of different cell wall thickness. Prior to the hydrocyclone trials, the pulp was screened to reduce its shive content. The hydrocyclone trials were carried out as a two-stage system, in which the reject from the primary stage was fed to the secondary stage and the accept from the secondary stage was fed back to the primary stage (Fig. 6). Five different mass reject rates (RRm) were used (19%, 27%, 45%, 72% and 91%), and the feed consistency of the primary stage was varied between 0.12 and 0.68%.

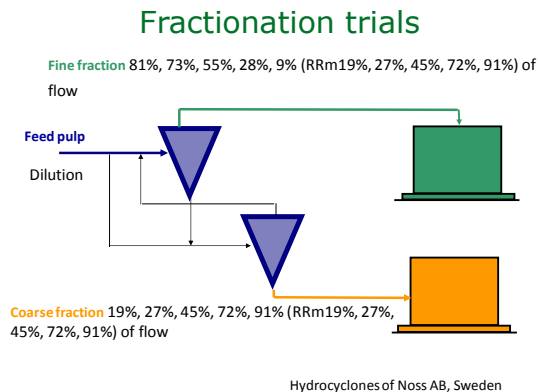


Figure 6. Trial configuration for hydrocyclone fractionation.

About 57–70% of the fines were removed from the accept fractions before the bleaching trials so as to obtain approximately the same fines content as in the reject fractions. Primary fines (4%) were removed using a rotating wire drum, Attisholz laboratory filter, with a 200-mesh (76 µm) wire.

5.2.2 Effect of birch kraft pulp primary fines on bleaching and sheet properties, Paper II

Primary fines (4%) were removed from an oxygen-delignified mill birch kraft pulp using Super DDJ (Dynamic Drainage Jar) equipment, which is composed of a tank with a 200-mesh wire (76 µm) and a mixer.

5.2.3 Reinforcing ability of fractionated softwood kraft pulp fibres, Paper III

5.2.3.1 Pressure screen

Screening was carried out at the KCL pilot plant with Valmet-Tampella TAP-50 pressure screen using wedge wire screen baskets. TAP-50 pressure screen has an axial feed manner. With this type of the screen, the rotor causes a negative pressure difference from feed to the accept. The rotor used in the trials was of C-type – a conical rotor body with connections to four foils. The screening was performed in one stage. The screening temperature was around 60°C, screening parameters are shown in Table 12.

Table 12. Screening conditions.

Aperture size mm	Open area (approximately) %	Con- sistency %	Flow rate l/s	rpm (rotor veloci- ty)	Volu- metric reject rate %	Mass reject rate %
#0.1	4.3	1.4	17.6	750	21.2	55

5.2.3.2 Hydrocyclone

The hydrocyclone trials were conducted in co-operation with Noss Ab. The hydrocyclone trials were carried out at the KCL pilot plant as a two-stage system, in which reject from the primary stage was fed to the secondary stage, and the accept from the secondary stage was fed back to the primary stage. The mass reject rate (RRm) was 19%. The feed consistency of the primary stage was 0.11%. Temperature in the trials was about 50°C.

5.2.4 Birch pulp fractions for fine paper and board, Paper IV

Birch pulp fractionation trials were carried out at KCL's pilot plant using hydrocyclones of Noss Ab and pressure screen (Valmet-Tampella TAP-50) equipped with smooth-hole screen basket of METSO having an aperture size of 0.2 mm. Hydrocyclone fractionation was carried out in two stages (Fig. 7), in which the reject from the primary stage was fed to the secondary stage, and accept from the secondary stage was fed back to the primary stage. A mass reject rate (RRm) of 80% was used. The feed consistency of the primary stage was 0.49%. Consistency of the accept pulp was 0.12% and that of the reject pulp was 3.5%. In the screening, one stage system was used. The objective in the screening was to remove only the finest material from the birch pulp, and for that reason as high a mass reject rate as possible was chosen for the trials. The mass reject rate was 94% and the feed consistency of the pulp was 1.3%, the consistency of the accept pulp was 0.07% and that of the reject pulp was 5.4%.

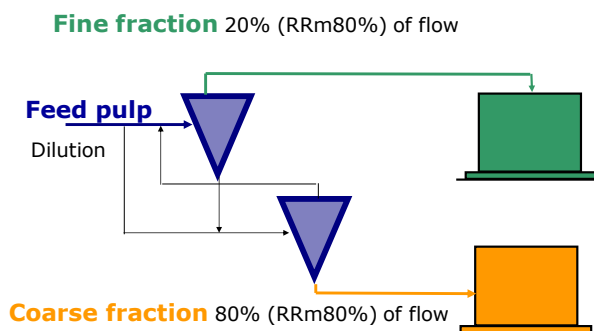


Figure 7. Trial configuration for hydrocyclone fractionation.

5.2.5 Evaluation of vessel picking tendency in printing, Paper V

The mill-dried pulps were allowed to swell overnight, and the next morning they were disintegrated using 50-litre disintegrator. The disintegration time was 15 minutes and the consistency 5%.

The pulps were fractionated using Bauer 3" hydrocyclone. Trials were performed with a feed pulp consistency of 0.1%, and the pressure difference was 1.6 bar. The trial configuration for *Eucalyptus globulus* is shown in Figure 8 and that for *Eucalyptus grandis* in Figure 9.

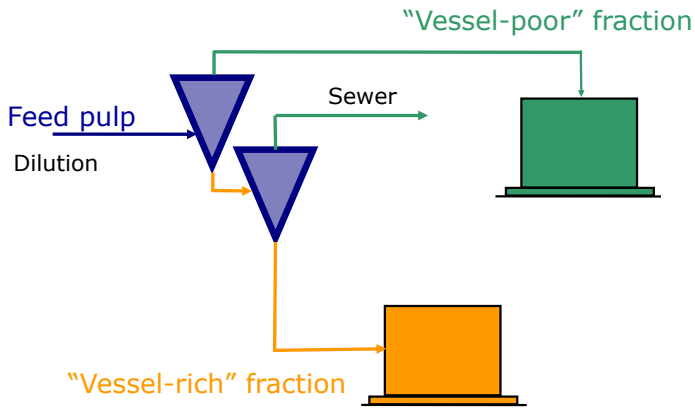


Figure 8. Trial configuration for *Eucalyptus globulus*.

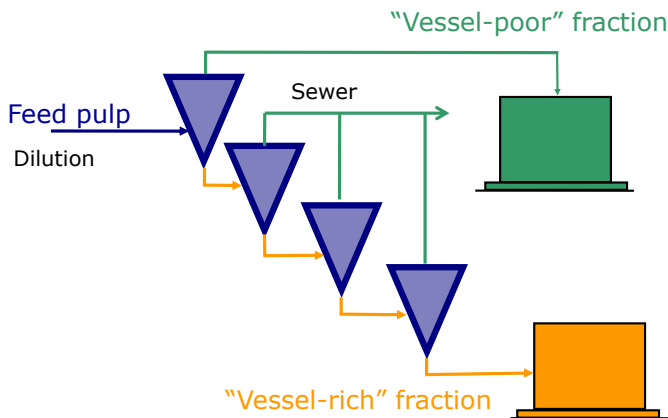


Figure 9. Trial configuration for *Eucalyptus grandis*.

Eucalyptus globulus was fractionated in a two-stage system (Fig. 8). The reject of the first stage was the feed of the second stage. The accept pulp from the second stage was not recovered. *Eucalyptus grandis* was fractionated in a four-stage system (Fig. 9). The reject of the first stage was the feed for the second stage, and the reject for the second stage was the feed of the third stage, etc. Also in this case the accept pulp from the second, third and fourth stages were not recovered.

After each fractionation stage the pulp samples were analysed with Kajaani FS-300, and the number of vessel elements, length and width was determined. This was done in order to monitor the separation efficiency.

5.3 Bleaching

5.3.1 Effect of cell wall thickness and fines on bleaching of softwood kraft pulp, Paper I

The unbleached fibre fractions (feed pulp, reject pulp, accept pulp containing all the fines and accept pulp from which fines were removed) were treated with oxygen, chlorine dioxide, hydrogen peroxide and ozone. Oxygen delignification was performed in steel autoclave bombs with air bath heating, ozone stage in a plastic flow-through reactor. The chelation stage, chlorine dioxide stage, alkaline extraction stage and hydrogen peroxide stage were carried out using sealed polyethylene bags in a thermostatic water bath. Washing between stages was always a standard laboratory washing: Pulp was diluted to 5% consistency with deionized water, whose temperature was the same as that of the preceding bleaching stage. After dewatering to a consistency of ~20%, the pulp was washed twice with cold deionized water with an amount equivalent to ten times the absolutely dry pulp amount.

The bleaching chemical treatments were carried out under the following conditions:

- Chelation (Q) before oxygen and hydrogen peroxide treatments: 70°C, 3% consistency, 60 min reaction time, EDTA 0.2% on pulp, initial pH was adjusted to 4.3. Pulp was washed after the chelation stage.
- Oxygen treatment (O): 90°C, 8% consistency, 30 min temperature increase time, 60 min reaction time, NaOH charge (% on pulp) 0.07 x incoming kappa number, 0.5% MgSO₄, oxygen pressure 8 bar. The final pH was from 10.8 to 11.6. Residual sodium hydroxide was determined by titration with hydrochloric acid.
- Chlorine dioxide treatment (D): 50°C, 8% consistency, 60 min reaction time, active chlorine charge 0.2 x incoming kappa number (%), initial pH was adjusted to ~ 3. Residual chlorine dioxide was determined by titration with sodium thiosulphate.
- Alkaline extraction (E) after chlorine dioxide and ozone treatments: 60°C, 10% consistency, 60 min reaction time, initial pH~11.
- Hydrogen peroxide treatment (P): 90°C, 10% consistency, 60 min reaction time, 2.0% NaOH on pulp, 0.25% MgSO₄ on pulp, 0.2% DTPA on pulp, 3.0% hydrogen peroxide on pulp. The final pH was from 9.4 to 9.6. Residual hydrogen peroxide was determined by titration with sodium thiosulphate.
- Ozone treatment (Z): 50°C, 12.5% consistency, 0.35% ozone on pulp, initial pH was adjusted to 3. The ozone formation was determined from potassium iodide solution by titration with sodium thiosulphate.

5.3.2 Effect of birch kraft pulp primary fines on bleaching and sheet properties, Paper II

The birch pulp and the fibre fraction were bleached in the laboratory using DEDeD sequence (e - neutralizing washing stage). Bleaching experiments were performed in a sealed plastic jar. The brightness target for the pulps was 88% ISO. The bleaching conditions are shown in Table 13.

Fines fraction was bleached using QQP and ZeQP sequence. Hydrogen peroxide and ozone were charged in such a way, that both the sequences had about the same bleaching chemical consumption calculated as OXE (oxidizing equivalents), 1780 OXE/kg. The conditions were as follows:

- Chelation (Q): 70°C, 2 % consistency, 20-30 min, EDTA 0.4-0.5% calculated on dry pulp, initial pH ~ 4.0.
- Hydrogen peroxide stage (P) in QQP sequence: 80°C, 15% consistency, 180 min, NaOH 2%, MgSO₄ 0.1%, H₂O₂ 4% calculated on dry pulp.
- Ozone stage (Z) in ZeQP sequence: ~50°C, 1.4% consistency, initial pH ~ 6. P-stage: NaOH 0.88%, H₂O₂ 1%, other conditions the same as in QQP.
- e-stage (neutralizing washing stage) in ZeQP sequence: 70°C, 2 % consistency, 10 min, initial pH 7.5-8.0.

Table 13. Bleaching conditions for the DEDeD sequence.

Stage	D0	E1	D1	e*	D2
Consistency, %	9	10	9	3	9
Temperature, °C	50	65	65		70
Reaction time, min	60	60	120	2	180
Final pH	<2.5	10.5-11.0	4.4	9.5	4.8
ClO ₂ charge, %	0.2 x incoming kappa number	-			According to the brightness after the D1
NaOH charge, %	-	0.4 x ClO ₂ charge in D0	0.085 x ClO ₂ charge in D1	0.4	-

*e-stage i.e. the neutralizing washing stage was performed straight away after the D1-stage.

5.4 Refining of the pulps, and testing of the pulps and handsheets

5.4.1 Reinforcing ability of fractionated softwood kraft pulp fibres, Paper III

The following analyses were conducted on all feed, accept and reject samples:

- Freeness value (ISO 5267-2).
- Water retention value, WRV, (SCAN C 62:00).
- Stock concentration (EN ISO 4119:1996).
- Length-weighted average fibre length, coarseness and fines using Kajaani FS-200 fibre analyser.
- Cell wall thickness measurement (Lammi 1997) for unrefined pulp only.
- Fibre wall width measurement (Lammi 1997) for unrefined pulp only.

5.4.1.1 Refining of the pulps

The pulps were refined in a Voith Sulzer LR1 research refiner. The pulps were refined with conical fillings 3-1.0-60C. The specific edge load was 2.5 Ws/m. Specific energy (SRE) levels were 0, 50, 100, 150 and 200 kWh/t. For the blend sheet trials the pulps were refined to the target tensile index of 70 Nm/g and 90 Nm/g.

Thin-walled and thick-walled fibre fraction were also refined separately using specific edge load of 1.5 Ws/m and 4.0 Ws/m, respectively. The specific refining energy of thin-walled fibre fraction was 75 or 150 kWh/t, and that of the thick-walled fibre fraction 60 or 200 kWh/t. The separately refined fractions were re-combined after refining and blended with GW. The kraft pulp share was either 25% or 45%.

5.4.1.2 Testing of the handsheet

Chemical pulp handsheets of 60 g/m² were prepared according to ISO 5269-1:1998.

In the blend sheets the kraft pulp share was either 25% or 45%, and no filler was added. The mechanical pulp used was either GW or TMP. Blend sheets of 60 g/m² were formed using recirculated white water according to ISO 5269-3:2008.

The tensile properties of the handsheets were measured according to EN ISO 5270:98, and apparent density according to ISO 534:05. The Scott bond was according to Tappi T833 modified, the light scattering coefficient according to ISO 2470-1:09, the air resistance (Gurley) according to ISO 5636-5, the tear index according to ISO 9416:09, and the fracture toughness test according to SCAN-P 77:95 modified.

5.4.2 Birch pulp fractions for fine paper and board, Paper IV

Fibre fractions were refined using a Voith Sulzer laboratory refiner and the physical properties of the handsheets were tested according to ISO, SCAN and Tappi standards. The feed pulp and the coarse fraction were refined using disk fillings 2/3-1.46-40D normally used for short-fibre pulps. The specific edge load was 0.5 Ws/m, the refining consistency was 4%, and the specific refining energy (SRE) levels were 0, 40, 80 and 120 kWh/t. In addition to this “normal” hardwood refining, the birch feed pulp, birch coarse fraction and birch fine fraction from hydrocycloning were refined using the following conditions:

- specific edge load (SEL) 0.2 Ws/m and consistency 4%, SRE 20 kWh/t
- SEL 0.2 Ws/m and consistency 5%, SRE 20 kWh/t
- SEL 0.4 Ws/m and consistency 5%, SRE 20 kWh/t
- SEL 0.5 Ws/m and consistency 4%, SRE 20 kWh/t

This was done in order to determine the effect of specific edge load and refining consistency on the pulp properties, especially on the tensile stiffness of the birch coarse fraction and Scott bond of the birch fine fraction.

For evaluation of bonding ability of the fine fraction, the birch fine fraction was blended with mill CTMP (CSF 470 ml), or with KCL pilot plant TMP (CSF 609 ml) after hot disintegration according to ISO 5263-2:2004. The fine fraction was used both unrefined and refined using disk filling 3-1.6-20D, SEL 0.5 Ws/m, and SRE 80 kWh/t. The laboratory sheets were made according to the ISO 5269-1:1998 conventional sheet-forming method.

5.5 Analyses

The following analyses were conducted on the pulp samples:

Analysis	Method	Paper
Kappa number	ISO 302	I, II
Viscosity	ISO 5351	I
Brightness after bleaching	Brightness was measured from the split sheet, ISO 2470	I, II
Fines content	Dynamic Drainage Jar (DDJ) with a wire hole diameter corresponding to a 200-mesh (76 µm) wire (Lammi 1997)	I, II
Cell wall thickness measurement		I
Simons' staining	(Simons 1959)	I
Total residual lignin, gravimetric and acid soluble lignin	KCL internal method TAPPI T222 modif.	II, IV, V
Uronic acids	An enzymatic hydrolysis followed by HPLC measurement (Tenkanen et al. 1995, Hausalo 1995)	II, IV, V
Carbohydrate composition	TAPPI T249, modif.	II, IV, V
Polysaccharide composition	Janson 1974	II, IV
Acetone soluble matter	SCAN-CM 49:03	II, IV, V
Post colour (PC)-number (80°C, 65% RH, 48h)	ISO 5630-3 by UV-Vis reflectance spectroscopy, KCL Internal method, described in (Liitiä et al. 2004)	II, IV
Calculation of cell type composition (fibres, vessels and ray cells)	SCAN-G3:90	V
The vessel length and width	Light microscope, 300 vessels were measured	V
Carboxyl group content	The method based on magnesium ion exchange. In principle, the bound magnesium ions are eluted and determined by quantitative analysis.	II, IV
Carbonyl group content	The oxime method. The carbonyl content is related to the nitrogen content as determined by the Kjeldahl procedure or elemental analysis.	II, IV
Metal content	Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-AES). The samples were dissolved in nitric acid in a microwave oven before the analysis.	II, IV

In addition to the above mentioned analyses, the following analyses were used:

- A technique based on total solubilisation of pulp by enzymatic hydrolysis was used (Tamminen et al. 1998). The lignin content, the content of phenolic hydroxyl groups and the content of conjugated groups were determined from the sample solution. (Paper I.)
- Wood extractives – free fatty acids, resin acids, lignans, sterols, steryl esters and triglycerides. The pulp sample was freeze-dried and extracted with acetone. The silyl derivative of the wood extractives was analysed using a gas chromatograph with a flame ionization detector (GC-FID). The amounts of free fatty acids, resin acids, lignans, sterols, steryl esters and triglycerides were determined as group sums. (Paper II).
- Vessel picking test (Paper V): The feed pulps, vessel-poor and vessel-rich pulps were used as unrefined. In addition, the vessel-rich fractions

were refined using a PFI-mill for 2,000 revolutions in order to see the effect of the refining on the vessels. Handsheets were formed according to standard EN ISO 5269-1 from the unrefined feed pulps, the vessel-poor and vessel-rich fractions and also from the refined vessel-rich fractions, five sheets for each sample. The target grammage of the sheets was 60 g/m². The handsheets were calendered with a sheet calender. The calendering conditions were as follows: line pressure of 94 kN/m (15 bar), 1 nip. The calendered laboratory sheets were taped to a carrier sheet. The sheets were printed with a 4-colour sheet-fed offset printing press using a commercial printing ink and one back-trap nip. Pick marks were collected from the blanket with adhesive tapes. The tapes were analysed with an image analyser to count the picking tendency: the total number of picks/cm² and the picked area μm . As the method is laborious no parallel measurement were done, so the reliability of the method cannot be properly estimated.

6. Results and discussion

6.1 Fibre and pulp properties of fractionated kraft pulps

Softwood and birch kraft pulp were fractionated using hydrocyclones and pressure screens, and eucalyptus kraft pulp using hydrocyclones. Softwood and birch kraft pulp were fractionated both as unbleached and bleached. In Chapters 6.1.1, 6.1.2 and 6.1.3, the fibre and pulp properties after the fractionation are presented.

6.1.1 Unbleached softwood pulp, Paper I

After the hydrocyclone treatment of unbleached softwood kraft pulp, pulps of different cell wall thickness were obtained. Figure 10 shows cell wall thickness of the feed (original pulp), accept (thin-walled) and reject (thick-walled) pulp for different mass reject ratios.

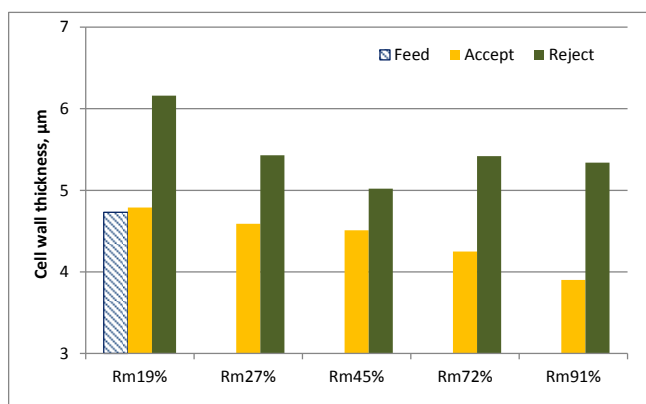


Figure 10. Cell wall thickness of the feed (original pulp), accept (thin-walled) and reject (thick-walled) pulp for different mass reject ratios.

Cell wall thickness varied from 3.9 µm to 6.2 µm (Fig. 10). The best separation of thickest wall fibres was achieved when the mass reject rate was 19%, and the best separation of thinnest wall fibres when the mass reject rate was 91%.

Figure 11 and 12 show the kappa number and brightness of the feed, accept and reject pulps plotted against fines content, respectively.

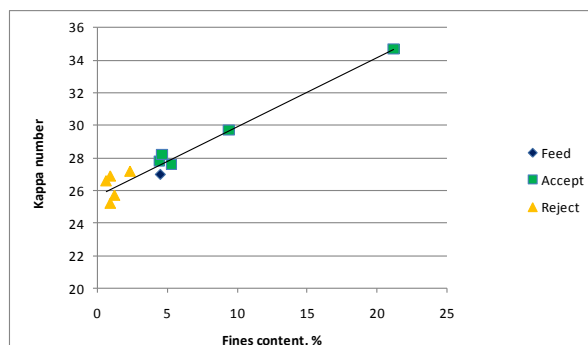


Figure 11. Kappa number of the feed, accept and reject pulps plotted against fines content.

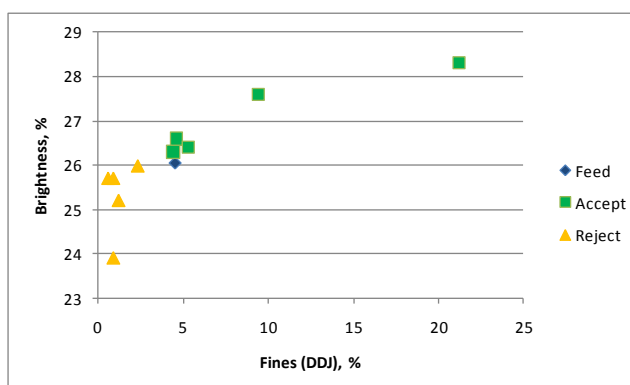


Figure 12. Brightness of the feed accept and reject pulps plotted against fines content.

Fines accumulated during fractionation in the thin-walled fibre (accept) fraction. The accumulated fines in the accept fraction had a higher lignin content and this increased the kappa number of the pulp (Fig. 11).

Despite the higher kappa numbers, the pulps having thin-walled fibres and a high fines content were brighter than the pulps having thick-walled fibres (Fig. 12) in agreement with Brännvall et al. (2007). One reason for this is that the hand sheets made from the pulp with thin-walled fibres and high fines content contained more fibres for a given weight, and as a result this sheet had more light-reflecting surfaces and consequently a higher light scattering coefficient.

The structure of the thin-walled and thick-walled fibres was clarified using Simons' staining method. Simons' staining reveals the structure of the fibre, the internal fibrillation and the looseness of the fibre wall. Simons' stain is a mixture of

two dyes, which have different molecular size. Orange dye is assumed to absorb to the fibre wall if there is enough space, and if the fibre wall is denser (smaller pores) the fibre is dyed blue since the blue dye have a smaller particle size (Simons 1959). Table 14 shows the results from Simons' staining.

Table 14. Simons' staining.

	Cell wall thickness µm	Orange %	Blue %	Undyed %
Feed (original pulp)	4.7	79	21	1
Thick-walled	6.2	45	54	1
Thin-walled	3.9	73	25	1

The structure of the thin-walled and thick-walled fibres was significantly different, as indicated by Simons' staining (Table 14).

The proportion of orange-dyed fibres was 45% for the pulp containing thick-walled fibres, and 73% for the pulp containing thin-walled fibres (Table 14). This means that the structure of the thick-walled fibres is denser than that of the thin-walled fibres. The structure of the feed pulp was about the same as that of the pulp containing thin-walled fibres, because the average cell wall thickness of the feed pulp was closer to that of the pulp containing the thin-walled fibres. The feed pulp contained more thin-walled fibres than thick-walled fibres.

6.1.2 Bleached softwood pulp, Paper III

Bleached softwood kraft pulp was fractionated according to fibre length using a wedge wire pressure screen, and according to cell wall thickness using hydrocyclone. Length-weighted average fibre lengths of the pulp fractions are shown in Figure 13.

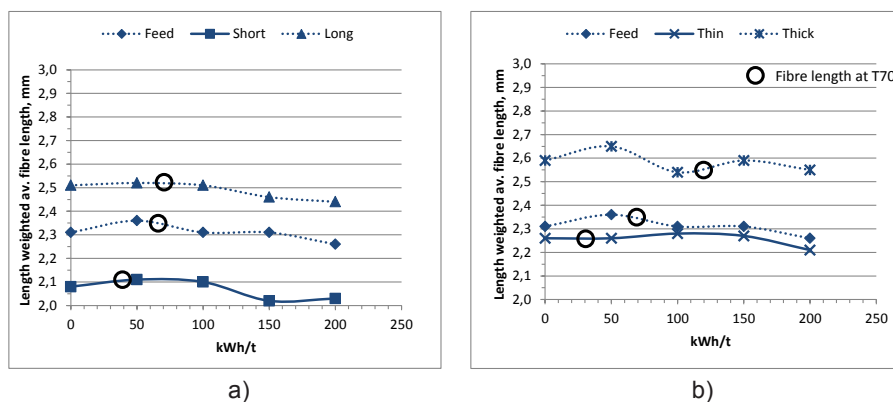


Figure 13. Length-weighted average fibre length of a) pressure screen fractionated and b) hydrocyclone fractionated pulps.

By single stage pressure screening with wedge wire screen baskets, a long fibre fraction with fibre length of 2.54 mm was obtained. The fibre length of the thick-walled fraction obtained by hydrocyclone fractionation was 2.59 mm, and the fibre length of the initial feed pulp was 2.31 mm.

Figure 14 shows the fibre length distributions of the pulp fractions.

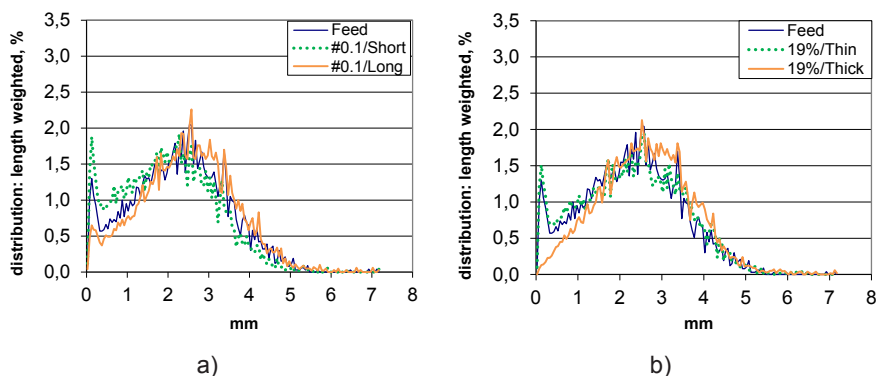


Figure 14. Fibre length distributions for pulps separated by a) pressure screen and b) hydrocyclone.

In the case of the pressure screen, the widths of the distribution curves are the same for the accept, reject and initial pulp. The distribution curve for the reject reached a peak in long fibres, and the distribution curve for the accept reached a peak in short fibres. With the hydrocyclone, the distribution curves coincided, indicating that the hydrocyclone did not actually separate the fibres according to length. The only difference in the curves is seen in the amount of the finest material (length < 0.5 mm).

Some fibre properties of the pulp fractions are shown in Table 15.

Table 15. Fibre properties of the pulp fractions.

	Coarseness mg/m	CWT µm	Fibre width µm	Approx. no. of fibres 10 ⁵ /g	Wet zero- span tensile strength at 50 kWh/t Nm/g
Feed	0.209	4.7	41.0	4.83	135
Pressure screen					
Short	0.196	4.1	40.0	6.80	133
Long	0.212	4.4	40.4	3.59	145
Hydrocyclone					
Thin	0.214	4.3	40.2	5.61	131
Thick	0.266	5.6	36.4	2.08	144

As already stated in Chapter 6.1.1 the hydrocyclone fractionated fibres according to the cell wall thickness, which was seen as a significant difference between the

cell wall thickness of the thin-walled and thick-walled fibre fractions, 4.3µm and 5.6µm, respectively (Table 15). Also, the difference in coarseness values of these pulps was substantial. In general, short-fibre fractions had the lowest coarseness values. The thin-walled fibre fraction and long fibre fractions had quite similar coarseness values to that of the feed pulp.

The wet zero-span tensile strength of long and thick-walled fibre fractions was higher than that of the other pulps. This indicates that long and thick-walled fibre fractions could possibly have fibres with high strength.

Table 16 shows some pulp and sheet properties of the fibre fractions at a tensile index of 70 Nm/g.

Table 16. Pulp and sheet properties of the fibre fractions at tensile index 70 Nm/g.

	kWh/t to T70	CSF ml	WRV g/g	Tear index mNm ² /g	Fracture toughness index Jm/g	Fracture toughness index T90 Jm/g	Scott Bond J/m ²	Scott Bond T90 J/m ²
Feed Pressure screen	72	578	1.88	16.3	25	24	402	650
Short	37	561	1.84	14.3	25	23	415	645
Long	67	636	1.84	18.0	26	26	260	402
Hydrocyclone								
Thin	28	593	1.82	15.5	24	23	343	500
Thick	135	591	1.91	17.9	23	27	288	506

The thick-walled fibre fraction had the poorest beatability; the energy input needed to a tensile index of 70 Nm/g was almost twice as high as that of the feed pulp. The short-fibre fraction and also the thin-walled fibre fraction were easier to refine than the feed pulp. The long fibre fraction had about the same energy need in refining as the feed pulp (Table 16).

Higher fibre length and also larger cell wall thickness is known to have a positive effect on tear strength (Paavilainen 1993, Kibblewhite 1982, Retulainen 1991). The tear strength of the long fibre fraction and also the thick-walled fibre fraction was better than that of the feed pulp (Table 16).

Both fibre length and bonding is known to influence fracture toughness (Seth 1996). The thick-walled fibre fraction with the highest coarseness had the poorest fracture toughness index at a tensile index of 70 Nm/g, which is in accordance with earlier studies (Seth 1996). The fracture toughness index of the thick-walled fibre fraction was increased substantially (from 23 Jm/g to 27 Jm/g), when it was further refined to a tensile index of 90 Nm/g, due to the increased bonding; the Scott bond of the thick-walled fraction was increased by 76% (from 288 J/m² to 506 J/m²) when refining to a higher tensile index.

6.1.3 Unbleached birch pulp, Paper II

Primary fines (4%) were removed from an oxygen-delignified mill birch kraft pulp using Super DDJ (Dynamic Drainage Jar) equipment, which is composed of a tank with a 200-mesh wire and a mixer. Table 17 shows the chemical composition of birch pulp, fibre fraction, and fines.

Table 17. Chemical Composition of birch pulp, fibre fraction, and fines fraction.

	Birch pulp	Fibre fraction	Fines fraction
Cellulose, %	71.7	73.8	43.4
Lignin, %			
Gravimetric	<2.0	<2.0	5.6
Soluble	0.6	0.5	0.6
Total			6.2
Xylan, %	26.1	24.6	48.3
Uronic acid composition			
Methyl glucuronic acid, mmol/kg	31	27	27
Hexenuronic acid, mmol/kg	78	69	91
Acetone extract, %	0.31	<0.05	1.55
Carbonyl groups, mmol/100 g	1.6	1.6	3.2
Carboxyl groups, mmol/kg	153.7	148.8	218.2

The fibre fraction and birch pulp had a higher cellulose content than the fines fraction, and the fibre fraction was extractives-free (Table 17). The fines fraction had a substantially higher content of lignin, xylan, extractives, and also hexenuronic acid. Also, the content of the carbonyl and carboxyl groups was higher in the fines fraction. A higher content of xylan, lignin, and carbonyl groups has also been reported earlier in the fines (Treimanis 2009; Treimanis et al. 2009; Bäckström and Brännvall 1999; Liitiä et al. 2001; Hinck and Wallendahl 1999; Heijnesson-Hulten et al. 1997; Westermarck and Capretti 1988). Ray cells are known to be a main source of extractives, and that is the reason for the higher content of extractives in the fines fraction (Heijnesson-Hulten et al. 1997).

Table 18 shows the content of various extractives components of the birch pulp, fibre fraction, and fines fraction.

Table 18. Content of extractives components of the birch pulp, fibre fraction, and fines fraction, analysed from freeze-dried pulps.

mg/kg	Birch pulp	Fibre fraction	Fines fraction
Fatty acids	170	26	1100
Betulinol	72	8	460
Lignan	39	10	540
Sterols	190	38	3000
Sterylesters	1200	310	25000
Triglycerides	72	42	760
Total	1700	430	31000

The fines fraction had a clearly higher content of various extractives components than the birch pulp or the fibre fraction (Table 18). Also, the proportion of the various extractives components of the fibre fraction, containing in practice no fines (0.4% of DDJ fines), was substantially lower than that of the birch pulp containing 4.6% of DDJ fines. In particular, the proportion of harmful betulinol, a main component in deposits or stickies found at both pulp and paper mills, was substantially lower in the fines-free fibre fraction. Also, the proportion of fatty acids and sterols were considerably lower, when the fines were removed.

Table 19 shows metal ion content of the fibre fractions.

Table 19. Metal ion content.

mg/kg	Birch pulp	Fibre fraction	Fines fraction
Copper	<0.5	<0.5	5.3
Iron	<3	<3	100
Magnesium	150	140	250
Manganese	100	69	350
Silica	65	42	220
Calcium	1500	1200	3700

The fines fraction had a clearly higher metal content than the birch pulp and the fibre fraction (Table 19). A high metal ion content of the fines fraction has also been revealed earlier (Westermarck and Capretti 1988; Treimanis 2009). As expected, the fibre fraction had a lower content of metal ions than the birch pulp.

In particular, the content of manganese, silica and calcium was lower in the fibre fraction than in the birch pulp. However, the positive thing was that the content of magnesium, a protector in hydrogen peroxide bleaching, was not much lower in the fibre fraction than in the original birch pulp.

6.1.4 Bleached birch pulp, Paper IV

Fractionation of bleached birch pulp using a hydrocyclone and pressure screen with a smooth-hole screen basket gave fractions with substantial differences in fibre and chemical composition. Table 20 and 21 shows the fibre and chemical composition of various fractions.

Table 20. Fibre composition of various fractions.

Fibre composition, (m/m) %	Feed	Hydrocyclone		Pressure screen	
		Fine	Coarse	Fine	Coarse
Fibres	96.1	84.5	97.1	45.6	97.3
Vessels	3.2	6.6	2.6	5.5	2.6
Ray cells	0.7	8.9	0.2	48.9	0.1

Table 21. Chemical composition of various fractions.

	Bleached pulp	Hydrocyclone		Screen	
		Fine	Coarse	Fine	Coarse
Cellulose, %	73.6	68.8	74.6	55.7	74.2
Lignin, %					
Gravimetric	+	0	+	1.3	+
Soluble	0.2	0.2	0.2	0.3	0.2
Total	0.2	0.2	0.2	1.7	0.2
Xylan, %	25.7	30.1	24.7	39.7	25.0
MeGlcA, mmol/kg	26	19	26	13	26
Acetone extract, %	0.09	0.38	+	0.87	0.06

+ = below the determination limit

Ray cells enriched to the fine fraction and due to this the content of extractives, lignin and xylan were higher in fine fraction (Bäckström and Brännvall 1999, Liittä et al. 2001, Hinck and Wallendahl 1999, Treimanis et al. 2009, Treimanis 2009).

Table 22 shows fibre dimensions of various fractions.

Table 22. Fibre dimension of various fractions.

Fibre properties	Feed	Hydrocyclone		Pressure screen	
		Fine	Coarse	Fine	Coarse
Fibre length, mm	0.93	0.80	0.96	0.67	0.92
DDJ fines, %	4.5	18.7	1.2	58.5	2.9
Cell wall thickness, μm	4.7	4.0	4.5	4.0	4.8
Fibre width, μm	20.5	18.9	20.0	18.8	20.0

There were no major differences in the fibre length of the hydrocyclone and screen coarse fraction and that of the feed pulp, Table 22. The fibre length of both the hydrocyclone and especially the screen fine fraction was lower than that of the feed pulp or the coarse fractions. The fine fractions also contained more fines than the feed pulp or the coarse fractions. In particular, the fines content of the screen fine fraction was significant high. The cell wall thickness and fibre width of both the hydrocyclone and screen fine fraction were a little lower than those of the feed pulp or the coarse fractions.

Table 23 shows pulp and sheet properties of various fractions.

Table 23. Pulp and handsheet properties of various fractions, unrefined pulps.

	Feed	Hydrocyclone		Pressure screen	
		Fine	Coarse	Fine	Coarse
Refining energy to T60, kWh/t	4	Not refined	16	Not refined	23
SR	18.0	48.0	15.0	90.7	15.5
WRW, g/g	1.80	2.08	1.68	n.d.	1.67
Tens. index, Nm/g	57.5	67.0	49.4	63.3	44.1
Scott bond, J/m ²	291	560	190	1452	226
Light scatt. coeff., m ² /kg	27.2	28.3	27.7	11.8	27.7
Air res., Gurley, s	4.9	137	1.9	>7200	1.9
Tens. stiff. ind. at SR23, kNm/g	6.94		7.75		7.13

n.d. = not determined, T60 tensile index 60 Nm/g.

Fine and coarse fraction exhibited clear differences in pulp and sheet properties, Table 23. Coarse fractions needed more refining energy to a certain tensile index than the unfractionated feed pulp. Fine fractions as unrefined already had a higher tensile index, Scott bond value, water retention value, and SR number than the reference pulp or the coarse fractions. Also, the sheet structure of the fine fractions was denser than that of the feed or coarse fractions. This was seen in the high air resistance values of the fine fractions.

The hydrocyclone coarse fraction had a higher tensile stiffness index at a given SR number than the reference feed pulp, Table 23.

6.1.5 Eucalyptus, Paper V

The bleached eucalyptus mill kraft pulps, *Eucalyptus globulus* from Southern Europe and *Eucalyptus grandis* from South America, were fractionated using Bauer 3" hydrocyclone.

Table 24 and Table 25 show cell type composition of the various fractions.

Table 24. Cell type composition of *Eucalyptus globulus*.

m/m, %	Feed	Vessel-poor	Vessel-rich
Fibres	96.5	97.4	98.4
Vessels	0.4	0.2	1.2
Ray cells	3.1	2.4	0.4

Table 25. Cell type composition of *Eucalyptus grandis*.

m/m, %	Feed	Vessel-poor	Vessel-rich
Fibres	96.7	95.5	96
Vessels	0.5	0.4	4.0
Ray cells	2.8	4.1	traces

The vessel elements were enriched to the reject fraction. Ohsawa et al. (1982) had also found that it is possible to separate vessel elements by hydrocycloning, and that the vessel elements are accumulated to the reject fraction.

When the hydrocycloning was performed in a two-stage system, Table 24, it was possible to increase the vessel content of the pulp from 0.4 % (m/m) to 1.2 % (m/m). In the four-stage system, the vessel content of the pulp increased from 0.5 % (m/m) to 4.0 % (m/m), Table 25. Somewhat better separation efficiency is found from the literature in Ohsawa et al. (1984). In their study, vessel elements were separated using a hydrocyclone; Centri-Cleacner 600, which is a more efficient hydrocyclone than the one used in this study, from eucalyptus pulp and they succeeded in enriching about 5.7 weight % of vessels to the reject fraction.

Table 24 and Table 25 show that the ray cells content of the vessel-poor fractions were higher than that of the vessel-rich fractions. In the case of *Eucalyptus grandis* the ray cell content of the vessel-poor fraction was even higher than that of the feed pulp. The enrichment of ray cells to the accept fraction has also been seen earlier (Panula-Ontto 2003).

Table 26 and Table 27 show that hydrocyclone separated the vessels according to their size.

Table 26. Vessel dimension of *Eucalyptus globulus*.

Vessel dimension, μm	Feed	Vessel-poor	Vessel-rich
Length	305	293	307
Width	178	153	190
Width/length	0.58	0.52	0.62

Table 27. Vessel dimension of *Eucalyptus grandis*.

Vessel dimension, μm	Feed	Vessel-poor	Vessel-rich
Length	357	346	368
Width	179	167	208
Width/length	0.50	0.48	0.57

The vessel-rich fractions had wider vessels than the other pulps. The length of the vessels was about the same in all the pulps. In addition, the vessels of the vessel-rich fractions were more square-shaped (width/length) than those of the feed pulp and those of the vessel-poor pulp. The same observation has also been made by Mukoyoshi et al. (1986).

The polysaccharide composition and the lignin content of the various pulps did not show any differences despite the enrichment of the vessels. The content of extractives was below the determination limit in all the cases. The only difference was seen in the content of hexenuronic acid. The *Eucalyptus grandis* vessel-rich pulp contained more hexenuronic acid (11 mmol/kg) than the *Eucalyptus grandis* feed pulp (7.2 mmol/kg) and the vessel-poor pulp (below determination limit, 4.5 mmol/kg). A higher xylan content of vessel rich pulp has been revealed earlier

(Figueiredo Alves et al. 2009), and it is known that methylglucuronic acid, the side group in native xylan, is partly converted into hexenuronic acid during kraft cooking (Teleman et al. 1995). Based on this information, it is likely that the vessel-rich fraction could have a higher hexenuronic acid content than the vessel-poor fraction. However, it should be kept in mind that this difference is not necessarily due to the vessel elements, because the vessel content of the vessel rich fraction was still fairly low, 4% (m/m).

6.2 Bleaching

Softwood kraft pulp was fractionated using hydrocyclones, and primary fines (4%) were removed from an oxygen-delignified mill birch kraft pulp using Super DDJ (Dynamic Drainage Jar) equipment. In Chapters 6.2.1, 6.2.2 and 6.2.3, the effect of fractionation on bleaching are presented.

6.2.1 Effect of cell wall thickness and primary fines on bleaching of softwood kraft pulp, Paper I

The overall effectiveness of various bleaching chemicals (i.e. bleaching chemical consumed per kappa number reduction and bleaching chemical consumed per brightness units gained) on unbleached softwood kraft pulp fibres of different cell-wall thickness was studied and the effect of primary fines on bleaching was investigated. Softwood kraft pulps of different average cell-wall thickness were obtained by fractionating with hydrocyclones. After the fractionation unbleached softwood kraft pulp fractions were treated with oxygen, chlorine dioxide, hydrogen peroxide and ozone.

Figure 15 shows the kappa reduction achieved by oxygen delignification as a function of cell wall thickness, and the consumption of sodium hydroxide per unit decrease in kappa number.

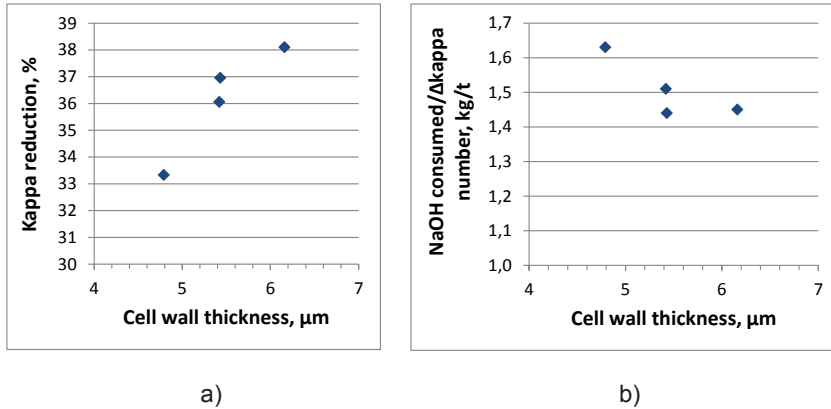


Figure 15. a) Kappa reduction in oxygen delignification as a function of cell wall thickness. b) NaOH consumption per kappa number reduction as a function of cell wall thickness. Fines content was from 1 to 1.9%.

In the oxygen stage kappa reduction increased (Fig. 15a) and the consumption of sodium hydroxide per kappa number unit decrease decreased (Fig. 15b) with the cell wall thickness at a given fines content. One possible explanation for these findings is that the proportion of S2 layer is greater in thick-walled fibres than in thin-walled fibres (Fengel 1969). According to the literature, the dissolution of lignin by oxygen is more effective from the S2 layer than from the (P+S1) or S3 layers (Wang et al. 2000, Laine 1996). It is known that oxygen predominantly reacts with lignin structures containing a free phenolic hydroxyl group. The concentration of phenolic hydroxyl groups in the lignin of the secondary wall of the fibres is more than double that found in the middle lamella and primary wall lignin (Hardell et al. 1980).

Figure 16 shows the contents of phenolic hydroxyl groups in the initial pulp, the pulp containing thick-walled fibres and the pulp containing thin-walled fibres.

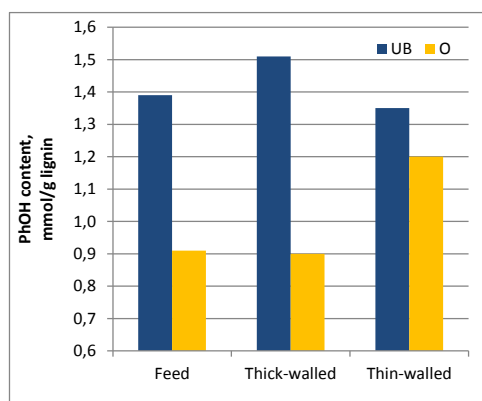


Figure 16. Concentration of phenolic groups in unbleached and oxygen-treated pulps. UB – unbleached, O – Oxygen delignified. Cell wall thickness: Feed 4.7 μm , Thick-walled 6.2 μm and Thin-walled 3.9 μm .

The pulp with thick-walled fibres contained more phenolic groups (Fig. 16), which are known to be formed during the cooking (Gellerstedt and Lindfors 1984). After the oxygen treatment, the number of phenolic groups was lower in the pulp containing thick-walled fibres than in the pulp containing thin-walled fibres. There may be differences in how the phenolic groups are morphologically located, i.e. differences in accessibility, phenolic groups in thick-walled fibres being more accessible than those in thin-walled fibres, and due to this the difference in the number of phenolic groups between thin-walled and thick-walled fibre fraction was detected.

Figure 17 shows active chlorine consumption per unit increase in brightness.

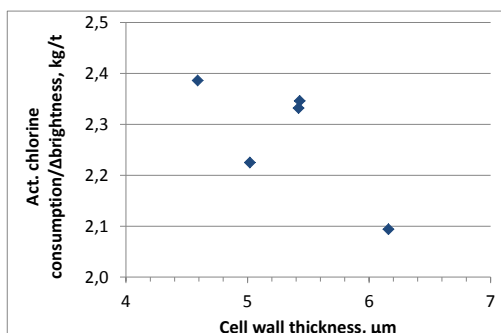


Figure 17. Active chlorine consumption kg/Δ brightness as a function of cell wall thickness. Brightness was measured after alkaline extraction stage. Fines content was from 1 to 1.7%.

A small correlation was seen between the cell wall thickness and the chlorine dioxide consumption per brightness unit gained (Fig. 17), the latter decreasing with cell wall thickness.

Laine (1996) found surface lignin playing a significant role with regard to brightness development during bleaching. He suggested that surface lignin is very probably more coloured than lignin in the other regions of the fibres. Also, Abe (1987) found that a prebeating, i.e. removal of surface lignin, improved bleachability of unbleached kraft pulp. Thin-walled fibres probably contain more lignin characteristic of surface lignin i.e. middle lamella lignin and precipitated lignin and this explains their poorer bleachability with chlorine dioxide. In addition, both Laine (1996) and Kleen et al. (1998, 2002) found that chlorine dioxide does not remove surface lignin effectively.

Figure 18 shows consumption of hydrogen peroxide per unit decrease in kappa number, and the number of conjugated groups, containing a carbonyl group.

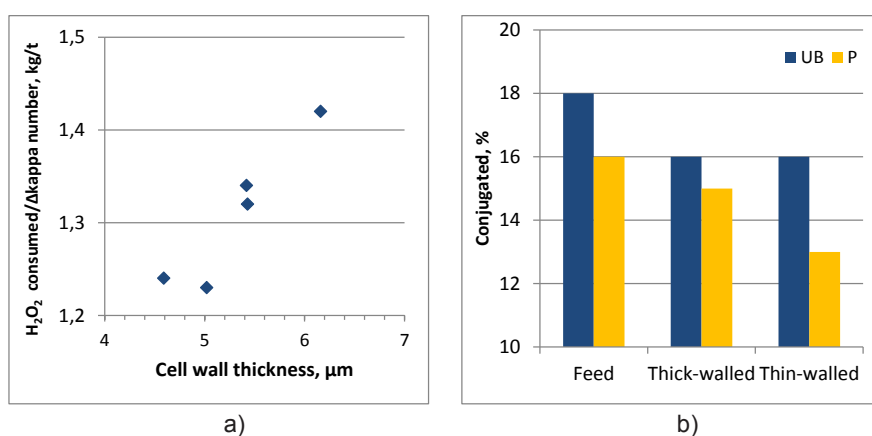


Figure 18. a) Hydrogen peroxide consumption/ Δ kappa number as a function of cell wall thickness. b) Amount of conjugated groups in unbleached and hydrogen peroxide-treated pulps. Fines content was from 1 to 1.7%. Pulps were chelated before the hydrogen peroxide treatment.

Consumption of hydrogen peroxide per unit decrease in kappa number increased with cell wall thickness at the same fines content (Fig. 18a). In addition, the number of conjugated groups, containing a carbonyl group, was reduced more by hydrogen peroxide treatment of the pulp containing thin-walled fibres than of the pulp containing thick-walled fibres (Fig. 18b). This also indicates that the hydrogen peroxide treatment was more effective on the pulp with thin-walled fibres. Thinner fibres have a higher fraction of the lignin on the surface; and the increased removal of conjugated structures from thinner fibres seems to be because the surface lignin is more accessible. Kleen et al. (1998, 2002) also found that peroxide cannot penetrate the fibre wall as well as chlorine dioxide and that hydrogen peroxide removes surface lignin effectively.

Figure 19 shows the consumption of hydrogen peroxide per brightness unit gained as a function of primary fines content of the pulp.

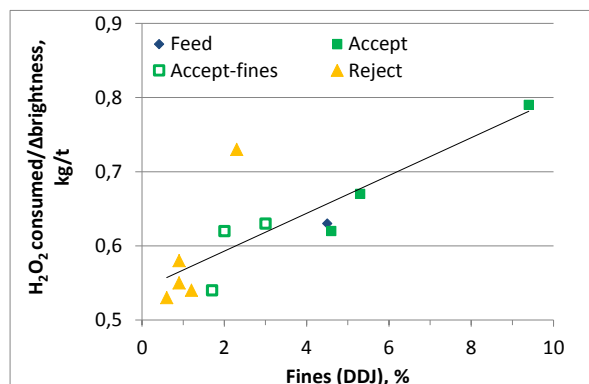


Figure 19. Consumption of hydrogen peroxide as a function of primary fines content.

The consumption of hydrogen peroxide per brightness unit gained increased with increasing fines content (Fig. 19), while metal content of the pulps was about the same. This might be caused by the differences in lignin content and structure (Bäckström and Bränvall 1999). According to Bäckström and Bränvall (1999) the better brightness gain achieved with no primary fines is due to the removal of chromophores.

Figure 20 shows the ozone consumption per brightness unit gained.

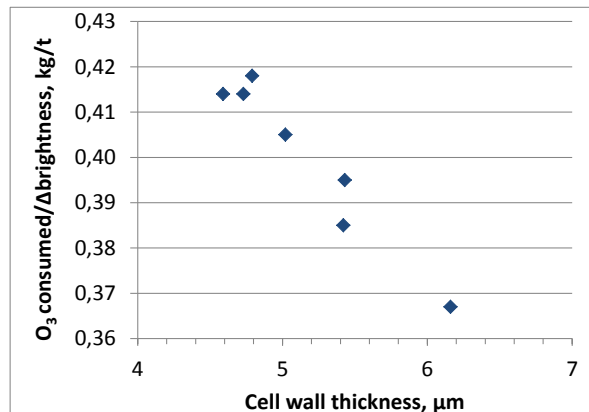


Figure 20. Ozone consumption/Δbrightness as a function of cell wall thickness. Brightness was measured after alkaline extraction stage. Fines content was from 1 to 1.9%.

The ozone consumption per brightness unit gained decreased with cell wall thickness (Fig. 20). The (P+S1) and S3 layers are said to react more quickly with ozone than the S2 layer (Wang et al. 2000). In the thin-walled fibres the proportions of (P+S1) and S3 layers are greater (Fengel 1969) and probably as a result

of this the consumption of ozone was higher in the pulp containing thin-walled fibres.

Figure 21 shows selectivity (Δ viscosity/ Δ kappa number) in ZE stage as a function of the fines content of the pulp.

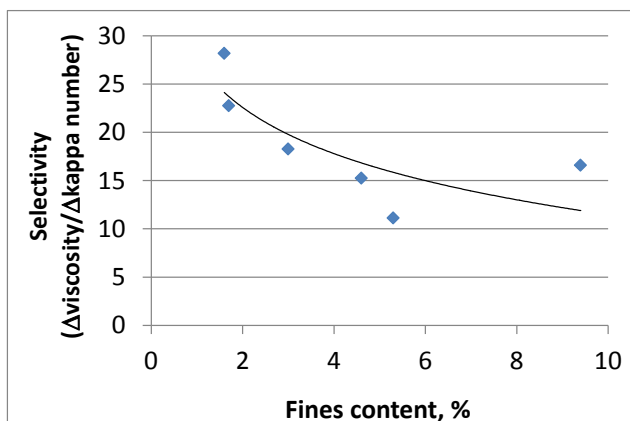


Figure 21. Selectivity (Δ viscosity/ Δ kappa number) in ZE stage plotted against fines content of the pulp.

The fines content seemed to have a slight influence on the selectivity values after the ozone treatment, so that the pulp containing a high amount of fines had a better selectivity (Fig. 21). The fines might have preserved the fibres, because, as mentioned earlier, ozone reacts more rapidly with outer cell wall material, (P+S1) and S3 layers, while reaction with lignin in the interior wall S2 appear to be slowed down by mass transfer limitations (Wang et al. 2000).

6.2.2 Effect of fines removal from birch pulp on the DEDeD bleaching efficiency, Paper II

Primary fines (4%) were removed from an oxygen-delignified mill birch kraft pulp using Super DDJ (Dynamic Drainage Jar) equipment, which is composed of a tank with a 200-mesh wire and a mixer.

Table 28 shows properties of the bleached birch pulp and birch pulp fibre fraction (fines removed).

Table 28. Kappa number and brightness of the bleached pulps and bleaching chemical consumption, and brightness before and after the aging treatment, and PC Number (465nm) for 48h, 80°C, 65% relative humidity.

	Birch pulp	Fibre fraction
Final kappa number	1.0	0.88
Final brightness, %	88.2	88.6
Active chlorine consumption, kg/BDt	46.37	43.60
Active chlorine consumption/ Δ kappa number, kg/BDt	3.93	3.96
Active chlorine consumption/ Δ brightness, kg/BDt	1.07	1.09
Brightness before treatment, %	88.61	88.46
Brightness after treatment, %	75.81	76.50
PC (Post Colour) number	3.13	2.86

Higher final brightness at 6% lower active chlorine consumption was obtained for the fines-free fibre fraction compared to the birch pulp. Calculated as active chlorine consumption per kappa unit reduction or brightness unit increase, there were no differences between the pulps, i.e. no difference in bleachability (Table 28).

A slight difference was seen in the brightness stability of the birch pulp and that of the fibre fraction. Brightness values before the aging treatment was about the same for both pulps (Table 28). However, after the aging treatment the birch pulp had a somewhat lower brightness value than the fibre fraction.

The PC number was affected by the content of lignin, hemicellulose component/uronic acids, extractives, and also the metal ions. The birch pulp had higher extractives content, and also higher hexenuronic acid content (although below the determination limit) than the fibre fraction. Also the UV-Vis spectra revealed that the fibre fraction had a lower content of hexenuronic acids and lignin, and also less C=O structures than the birch pulp (Fig. 22).

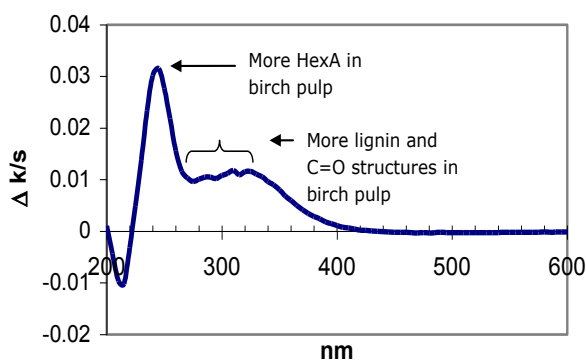


Figure 22. Difference between the UV-Vis spectra of the birch pulp and the fibre fraction.

6.2.3 Effect of the QQP and ZeQP bleaching of the birch fines fraction on the extractives, Paper II

The birch fines fraction was treated using QQP and ZeQP sequences.

Table 29 shows extractives content of the fines fraction and QQP bleached fines fraction.

Table 29. Extractives content of the fines fraction and QQP bleached fines fraction.

	Unbleached Fines fraction	QQP bleached Fines fraction	ZeQP bleached Fines fraction	
mg/kg			Ze	ZeQP
Fatty acids	1100	2200	1100	2000
Betulinol	460	520	370	400
Lignan	540	680	450	660
Sterols	3000	3000	2200	2500
Sterylesters	25000	25000	13000	13000
Triglyserides	760	790	760	770
Total	31000	32000	18000	19000

Table 29 shows, that the hydrogen peroxide, QQP bleaching, was unable to remove the extractives from the birch fines fraction although it acts also as an alkaline extraction stage. ZeQP bleaching decreased the total content of extractives from 31000 mg/kg to 19000 mg/kg. The extractives content of the fines fraction was about 42% lower after the Ze bleaching than that of the unbleached fines fraction, and after the ZeQP sequence about 40% lower. However, the content of some extractives components after the hydrogen peroxide stage in ZeQP bleaching was about the same or even greater than in the unbleached fines. The content of sterylesters was substantially lower after the bleaching than before that. The content of sterols was slightly lower in ZeQP bleached fines than in the unbleached fines. Barbosa et al. (2008) also found ozone to be effective in removing sterols in the bleaching of Eucalyptus kraft pulp.

It is known that the problems with birch extractives have anatomical and chemical explanations (Back and Allen 2000, Sjöström 1981, Laamanen 1984). In birch the majority of the extractives are located inside the parenchyma cells, which have rather small pits. This renders the birch pulp extractives more troublesome than in other hardwoods. Similar to what was earlier found by Laamanen (1984), hydrogen peroxide treatment of birch kraft pulp in the laboratory, with a large dose of 5%, did not change the composition of the extractives. The reason for this was said to be that hydrogen peroxide was unable to penetrate into the (extractives) parenchyma cells. Furthermore, in the alkaline hydrogen peroxide stage, in which there are significant concentrations of Ca^{2+} - and Mg^{2+} - ions, the fatty acids will form metal soaps rather than soluble fatty acids soaps, and due to this the extractives content will not decrease (Fernando and Daniel 2005). In addition, it has been observed that the sterols remaining in bleached pulps are present almost exclusively inside the parenchyma cells (Fernando and Daniel 2005). It is also men-

tioned in the literature (Fernando and Daniel 2005) that betulinol and saturated fatty acids are very resistant towards oxidation.

6.3 Properties of fractionated softwood and birch kraft pulps in the mixture with softwood kraft or mechanical pulp

Bleached softwood and birch kraft pulp were fractionated using hydrocyclones and pressure screens. In Chapters 6.3.1–6.3.4, the properties of fractionated softwood and birch kraft pulps in the mixture with mechanical or softwood kraft pulp are presented.

6.3.1 Reinforcing ability of fractionated softwood kraft pulp fibres, Paper III

Reinforcement capacity of the feed pulp, thick-walled fibre fraction obtained by hydrocycloning and long fibre fraction obtained by wedge wire pressure screening were compared in the mixture with two types of mechanical pulp, GW and TMP.

Figure 23 shows freeness values of blend sheets and Figure 24 shows tear index values of the blend sheets.

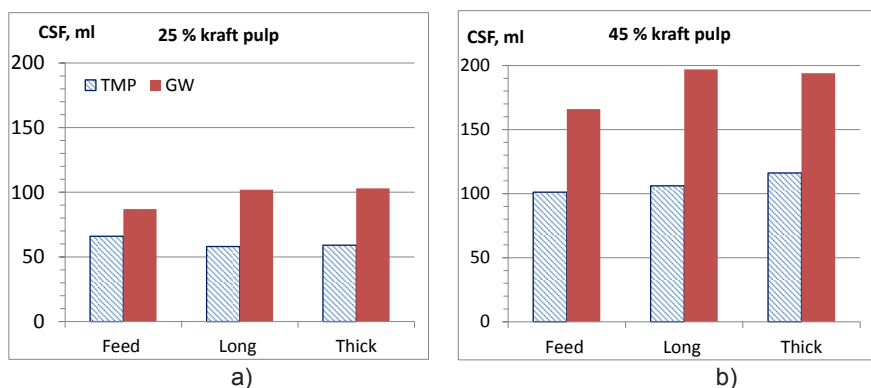


Figure 23. Freeness values of blend sheet with kraft pulp proportion 25% a) and 45% b).

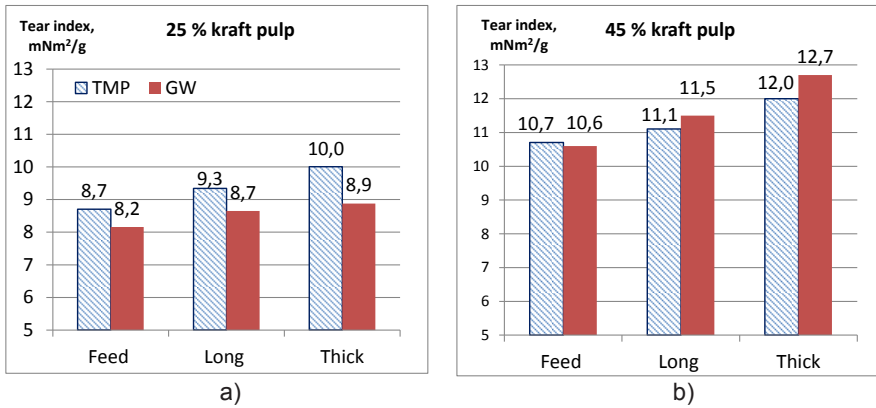


Figure 24. Tear index values of blend sheet with kraft pulp proportion 25% a) and 45% b).

When the various chemical pulps were refined to the given tensile index, the thick-walled and the long fibre fraction gave, in the mixture with GW, substantially higher freeness than the feed pulp. For the mixture with TMP, the trend was not that clear (Fig. 23).

The greatest differences regarding strength properties were seen in the tear index of the blend sheets when the chemical pulp was refined to the tensile index of 70 Nm/g (Fig. 24). The thick-walled fibre fraction gave clearly higher tear index values than the feed pulp in the mixture both with GW and TMP. Also, the long fibre fraction gave somewhat higher tear index values, especially when mixed with GW and when the kraft pulp content was 45%. The GW pulp had shorter fibres and a poorer tear index than the TMP pulp, and in this case the chemical pulp with long and strong fibres increased the tear index of the GW mixture.

Figure 25 shows fracture toughness index of the blend sheets.

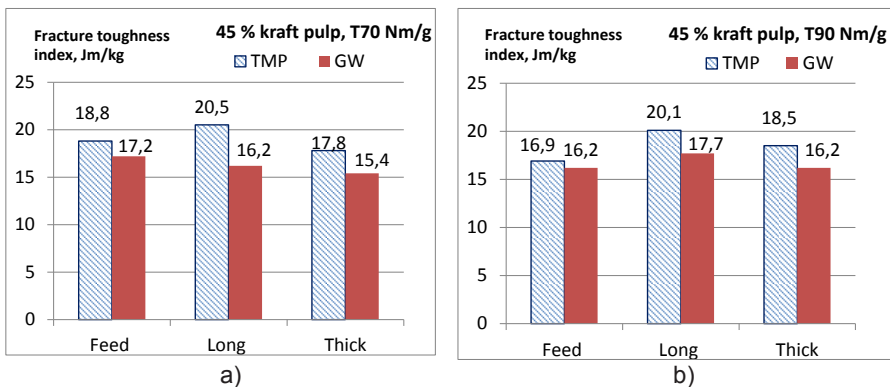


Figure 25. Fracture toughness values of blend sheet with kraft pulp proportion 45% at tensile index 70 Nm/g a) and 90 Nm/g b).

Fractionating the chemical pulp according either to cell wall thickness or fibre length did not show any positive effect on the fracture toughness index of the pulp mixture. At a tensile index of 70 Nm/g, the thick-walled fibre fraction gave even poorer fracture toughness values in the mixture than did the feed pulp (Fig. 25a). Fracture toughness index of the thick-walled fibre fraction and mechanical pulp mixture was improved with further refining of the chemical pulp to tensile index of 90 Nm/g, i.e. with increased bonding (Fig. 25b). The long fibre fraction refined to a tensile index of 90 Nm/g gave a better fracture toughness index than the feed pulp (Fig 25b). It has been reasoned that long, ductile and low stiffness fibres should enhance the fracture toughness of paper at all concentrations (Alava and Niskanen 1997). A mixture of more than one kind of reinforcement fibre pulp (hybrids) may also improve paper properties (Alava and Niskanen 1997); these results are in good accordance with the mentioned statements.

6.3.2 Reinforcement capacity of separately refined thin- and thick-walled fibre fractions, Paper III

Thin- and thick-walled fibre fractions were refined separately using a specific edge load of 1.5 Ws/m and 4.0 Ws/m, respectively. Specific refining energy of thin-walled fibre fraction was 75 or 150 kWh/t, and that of the thick-walled fibre fraction 60 or 200 kWh/t. After the refining the fractions were re-combined, the mixing proportion was the same as in the fractionation, i.e. ~80% of the thin-walled fraction and ~20% of the thick-walled fraction. Separately refined and after refining the re-combined fractions were then blended with GW; the share of kraft pulp was either 25% or 45%.

Figure 26 shows freeness values of the GW blend sheets.

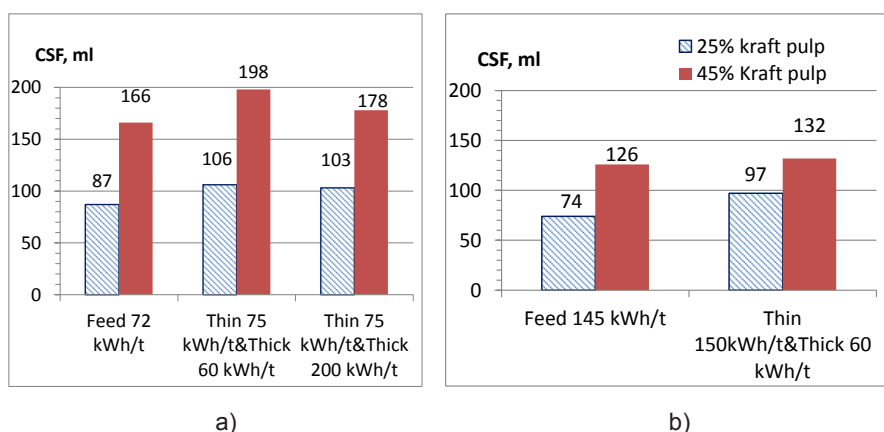


Figure 26. Freeness values of the GW blend sheets. Kraft pulp proportions of 25% and 45%, Thin and Thick fraction were refined separately and after the refining re-combined.

Separately refined fibre fractions in all cases gave a higher freeness of the chemical pulp-GW mixture than the feed pulp-GW mixture (Fig. 26).

Figure 27 shows tear index of GW blend sheets, and Figure 28 fracture toughness of the GW blend sheets.

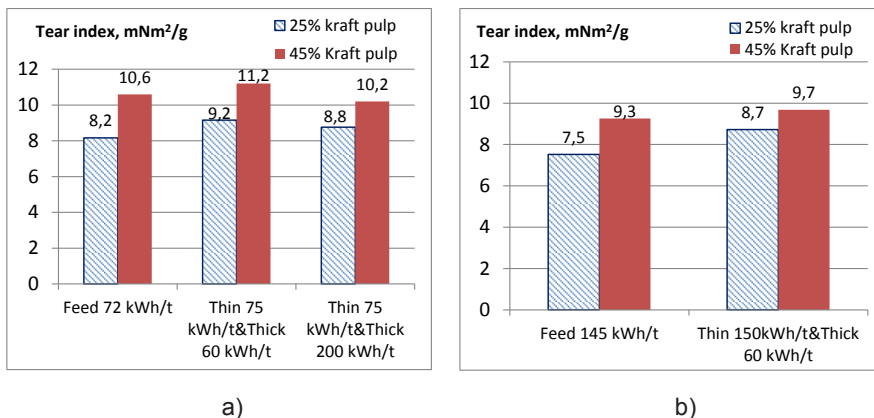


Figure 27. Tear index values of the GW blend sheets. Kraft pulp proportion 25% and 45%, Thin and Thick fraction were refined separately and after the refining re-combined.

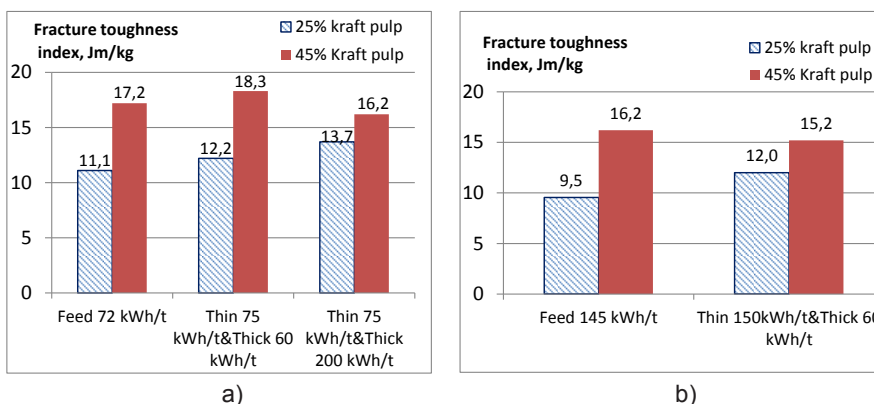


Figure 28. Fracture toughness values of the GW blend sheets. Kraft pulp proportions of 25% and 45%, Thin and Thick fraction were refined separately and after the refining re-combined.

When the share of the chemical pulp was 25%, the separately refined fractions gave a better tear index and also fracture toughness values in the mixture with GW than the feed pulp (Fig. 27 and 28). Then the thick-walled fibre fraction could be refined with a higher energy input, 200 kWh/t, without significantly reducing the tear strength of the mixture (Fig. 27a). In addition, the fracture toughness of the

mixture was then substantially higher than that obtained when the thick-walled fibre fraction was refined with lower energy input, 60 kWh/t (Fig. 28a).

Also, the thin-walled fibre fraction could be refined with a higher energy input (Fig. 27b and 28b), and still better tear strength and fracture toughness were obtained than with the feed pulp in the mixture. However, the higher energy input in the refining of the thin-walled fibre fraction did not have any positive impact on the fracture toughness of the mixture (Fig. 28b).

When the chemical pulp share was higher, 45%, the separately refined fractions gave better tear and fracture toughness values when the thick-walled fibre fraction was refined with a lower energy input (Fig. 27a and 28a).

From the results it can be concluded that, when the kraft proportion was low (25%), refining of the thick walled fibre fraction with a higher energy input gave similar or even better properties than those obtained when refined with lower energy input (Fig. 27a and 28a). Also, the thin-walled fibre fraction could be refined with a higher energy input, and still better results were obtained when compared to the feed pulp refined with a specific refining energy of 72 kWh/t (Fig. 27b and 28b). When the kraft proportion was higher, 45%, it was better to refine the thick-walled fibre fraction with lower energy input, 60 kWh/t (Fig. 27a and 28a).

The results obtained are in accordance with earlier studies; Mohlin et al. (1983), Mohlin et al. (1989) and Levlin (1990) have found that, when the chemical pulp share in the paper is less than 20–30% of fibres, it can clearly be refined over its maximum tear strength in order to improve the tensile strength of chemical pulp and paper without reducing the tear strength or fracture toughness of the paper.

6.3.3 Birch coarse fraction and pine kraft pulp mixture, Paper IV

For the evaluation of the board top layer and fine paper, the birch coarse fraction obtained by hydrocyclone fractionation and mill pine kraft pulp were mixed together. The birch pulp was refined to the SR value of 23, and the pine kraft pulp to the SR value of 25.

One of the desirable properties of the board is a high bending stiffness ($S_b = Et^3/12$). It is dependent upon the modulus of elasticity (E) and the thickness (t) of the paperboard. The construction of paperboard is, therefore, usually a bulky middle ply and outer ply with high modulus of elasticity or tensile stiffness. One way to increase the bending stiffness is to increase the tensile stiffness of the outer plies. It should be kept in mind that, if each surface layer is 5% of the paper thickness, then doubling their elastic modulus raises the bending stiffness by only 27%. Thickness has a greater influence on bending stiffness than the elastic modulus (Kajanto 1998).

Figure 29 shows tensile stiffness of the pulp mixtures.

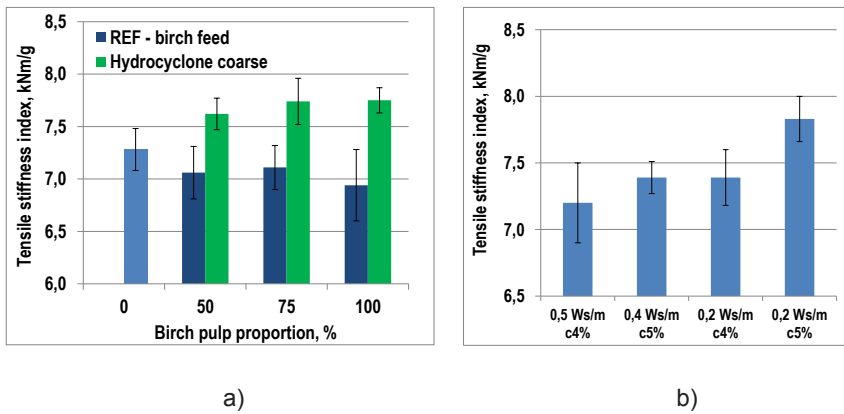


Figure 29. a) The tensile stiffness index of the pulps at various birch pulp proportions with standard deviations. b) Tensile stiffness index of hydrocyclone coarse fraction with standard deviations. The specific edge load was 0.5 Ws/m, 0.4 Ws/m and 0.2 Ws/m. Refining consistency was 4% and 5%. Specific refining energy was 20 kWh/t.

Fractionation of bleached birch pulp with hydrocyclone gave a coarse fraction which had a considerably higher tensile stiffness at a given SR number than the unfractionated reference pulp (Fig. 29a). However, the coarse fraction needed more refining energy to the target SR number than the unfractionated pulp, 49 kWh/t vs. 26 kWh/t, respectively.

By reducing the specific edge load in the refining from 0.5 Ws/m to 0.2 Ws/m, and increasing the refining consistency from 4% to 5%, it was possible to further improve the tensile stiffness of the hydrocyclone coarse fraction (Fig. 29b).

Figure 30 shows the roughness (Bendtsen) of the handsheets measured from the top side.

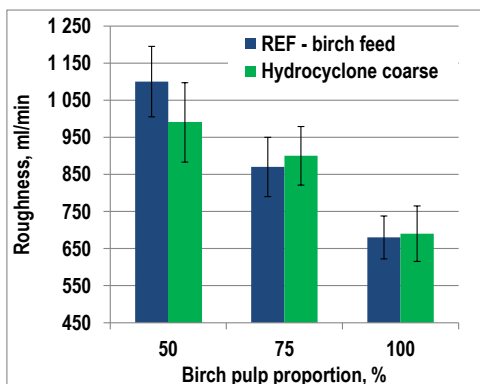


Figure 30. Roughness (Bendtsen) of the handsheets measured from the top side with standard deviations.

The smoothness/low roughness is an important property of paper and board top layer, as it affects the need for calendering and coating, and finally the printability. In this study, as expected, roughness of the handsheet decreased with increasing birch kraft pulp content. The birch feed pulp and birch coarse fraction gave about the same roughness values of the blend sheet, Fig. 30.

6.3.4 Birch fine fraction and mechanical pulp mixture, Paper IV

For the evaluation of the board middle layer, the birch fine fraction and mill CTMP (CSF 470 ml) were mixed together. The reference furnish was CTMP-pine kraft pulp mixture (75:25). The birch fine fraction was blended with the CTMP pulp unrefined or after refining with 80 kWh/t. In the blend sheets the birch pulp proportion was 25% or 20%, and no filler was added.

Figure 31 shows Scott bond vs. bulk of the various pulp mixtures.

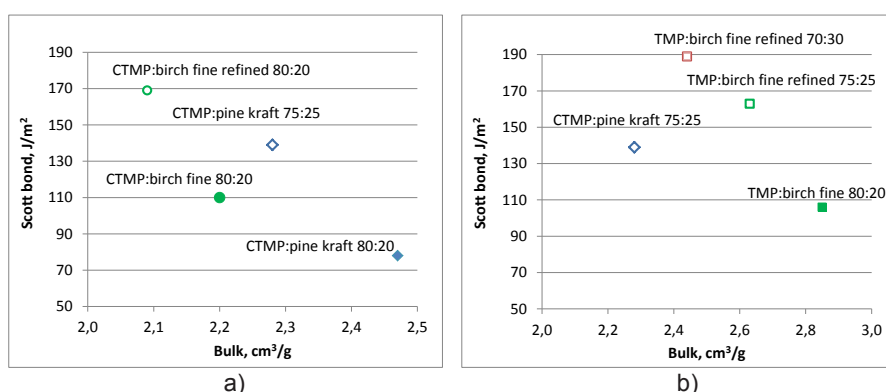


Figure 31. Scott bond vs. bulk of a) blend of CTMP, pine pulp and birch fine fraction and b) blend of TMP, pine pulp and birch fine fraction.

The refined birch fine fraction substantially increased the bonding measured as Scott bond (Fig. 31a). The results indicate that a coarser CTMP could be used, resulting in an increase of bulk, but with still an acceptable bonding. Based on the above-mentioned result, the hydrocyclone birch fine fraction was also blended with coarser mechanical pulp (TMP CSF 609 ml), aiming at increasing the bulk without losing the Scott bond of the fine fraction-mechanical pulp mixture (Fig. 31b).

Compared to the reference mixture (CTMP 75 % and pine kraft pulp 25%), a 25% higher bulk was obtained with the TMP-unrefined birch fine fraction (80:20) mixture. However, the Scott bond value of the TMP-unrefined birch fine fraction mixture (80:20) was lower by 24%. When the refined birch fine fraction proportion was either 25% or 30% in the mixture, substantially higher bulk values were obtained compared to the reference mixture – 2.63 cm³/g (15% higher) and 2.44 cm³/g (7% higher), respectively. Also, the Scott bond values of the refined birch fines and TMP mixture were higher than that of the reference. The Scott bond

value of the mixture, TMP 75% – refined birch fine fraction 25%, was 163 J/m², i.e. 17% higher than that of the reference, and the Scott bond value of the mixture, TMP 80% – refined birch fine fraction 20%, was 189 J/m², i.e. 36% higher than that of the reference.

6.4 Evaluation of vessel picking tendency of Eucalyptus pulp, Paper V

The bleached mill eucalyptus kraft pulps, *Eucalyptus globulus* from Southern Europe and *Eucalyptus grandis* from South America, were fractionated using Bauer 3" hydrocyclone. The vessel-rich pulps were refined in a PFI-mill (refining consistency 10%) for 2000 revolutions and after the refining the picking tendency was determined. The vessel picking tendency was analyzed by printing the handsheets with a full scale printing machine, a 4-colour sheet-fed offset printing press, and using a commercial printing ink.

Table 30 shows the vessel content of the unrefined and refined *Eucalyptus grandis* vessel-rich pulp and Table 31 shows the vessel dimensions of the fractions. In Figure 32 is a light microscope picture taken of the refined vessel-rich fraction.

Table 30. Vessel content of the unrefined and refined vessel-rich pulp, *Eucalyptus grandis*.

m/m, %	Unrefined vessel-rich	Refined vessel-rich
Fibres	96	95.1
Vessels	4.0	4.9
Ray cells	traces	-

Table 31. Vessel dimension in vessel-rich pulp fraction of *Eucalyptus globulus*.

Vessel dimension, µm	Unrefined vessel-rich	Refined vessel-rich
Length	307	334
Width	190	171
Width/length	0.62	0.51

The calculation of the vessel elements showed higher values after the refining (Table 30), because the vessels were broken and split in the refining (Fig. 32). This was also seen in the vessel dimensions and shape of the vessel elements. The width/length ratio was lower, which means that the vessels were not as square-shaped as before the refining (Table 31).



Figure 32. Refined vessel-rich fraction of *Eucalyptus globulus* pulp.

It is known from the literature (Ohsawa et al. 1984) that especially high consistency refining is effective for vessel element destruction, and that it can reduce the content of large vessel elements considerably. Regardless of refining methods, the destruction of vessel elements reaches a certain level at CSF 400 ml, and further refining results in only small change in the size of the vessel element (Nanko et al. 1988). According to Nanko et al., high consistency refined pulp contained more fibrillated fibres and fibrillated vessels. However, fibrillation of vessel elements cannot be detected in this study (Fig. 32).

Figures 33 and 34 show the picture taken from the printed handsheets made from the unrefined and the refined vessel-rich fraction, *Eucalyptus globulus* and *Eucalyptus grandis*, respectively. Table 32 and 33 show vessel picking results for *Eucalyptus globulus* and *Eucalyptus grandis* pulp fractions, respectively.

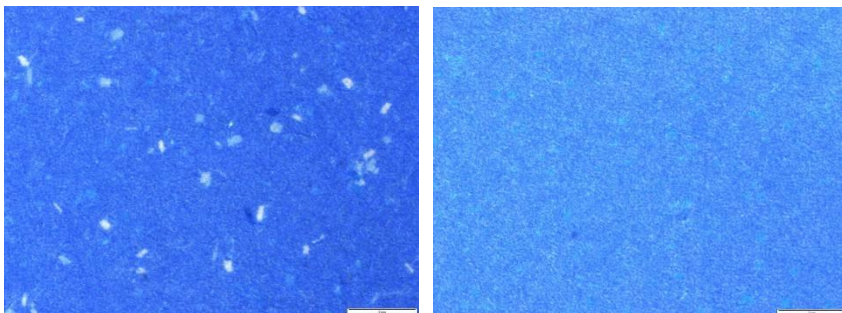


Figure 33. Printed handsheet made from unrefined (on the left) and refined (on the right) *Eucalyptus globulus* vessel-rich fraction.

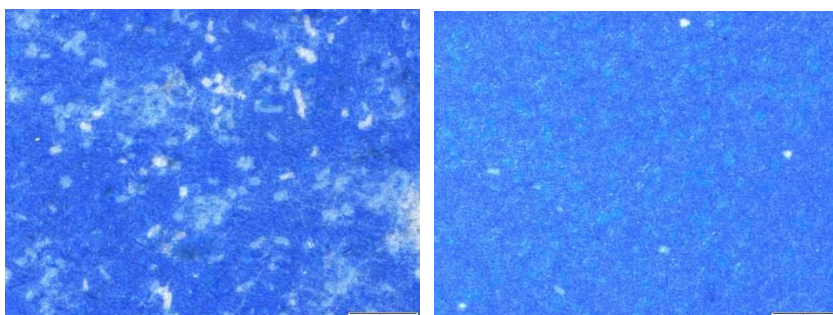


Figure 34. Printed handsheet made from unrefined (on the left) and refined (on the right) *Eucalyptus grandis* vessel-rich fraction.

Table 32. Vessel picking results for *Eucalyptus globulus* feed pulp, vessel-poor, unrefined and refined vessel-rich fraction.

Number of picks/cm ²	Feed	Vessel-poor	Unrefined vessel-rich	Refined vessel-rich
Ink	4.1	3.0	16.2	1.2
Back trap	2.2	1.7	10.8	1.1
Total	6.4	4.7	27.0	2.3
Picked area, μm ²				
Ink	0.19	0.12	1.09	0.03
Back trap	0.04	0.03	0.35	0.02
Total	0.23	0.15	1.44	0.05

Table 33. Vessel picking results for *Eucalyptus grandis* feed pulp and refined vessel-rich fraction.

Number of picks/cm ²	Feed	Refined vessel-rich
Ink	3.2	4.2
Back trap	2.1	2.8
Total	5.3	7.0
Picked area, μm ²		
Ink	0.20	0.22
Back trap	0.06	0.10
Total	0.26	0.32

By refining the *Eucalyptus globulus* vessel-rich fraction, the number of picks/cm² was reduced from 27.0 picks/cm² to 2.3 picks/cm² (Table 32). Reduced picking is also seen in Fig. 33, which shows how the number of picked areas was substantially lower in the refined pulp. Picked areas are shown as white spots in the handsheet.

After the refining, the number of picks/cm² was lower than that in the unrefined feed pulp, and even lower than that in the vessel-poor pulp. The number of picks/cm² of the *Eucalyptus globulus* feed pulp, vessel-poor pulp and refined ves-

sel-rich fraction was 6.4, 4.7 and 2.3, respectively. Also, the picked area decreased remarkably in the refining, from $1.44 \mu\text{m}^2$ to $0.05 \mu\text{m}^2$, and it was lower than that of the feed pulp ($0.23 \mu\text{m}^2$) and that of the vessel-poor pulp ($0.15 \mu\text{m}^2$).

The number of picks/cm² and the picked area also decreased in the refining of *Eucalyptus grandis* vessel-rich fraction. However, the total number of picks/cm² of the refined *Eucalyptus grandis* vessel-rich fraction was 7.0 (Table 33). This is still about 30% higher than that of the feed pulp. Also, the total picked area was about 20% higher for the refined vessel-rich fraction than that of the feed pulp. In addition, Fig. 34 shows that refined *Eucalyptus grandis* pulp still contained picked areas.

The picking tendency of refined vessel-rich pulp was reduced because the vessels were broken (Figure 32) in the refining, and for that reason they were as much square-shaped as before the refining. In addition, the conformability of the fibres was increased in the refining, and vessel-to-fibre bonding strength was also increased (Ohsawa et al. 1984, Ohsawa 1988, Colley 1975).

6.5 Applicability of fractionation

Fibre fractionation gives more advanced possibilities to design pulps with unique fibre characteristics. In this study, softwood and hardwood fibres were separated according to different principles when using different types of fractionating equipment.

6.5.1 Softwood

According to the results for pure softwood chemical pulp, the long fibre fraction obtained by wedge wire pressure screening would be optimal for reinforcement pulp. It was easy to refine, and had long fibres, a good tear index and fracture toughness, and also better drainage than the unfractionated reference pulp according to freeness and WRV values. Thick-walled fibre fraction also had long fibres and good strength properties, but the need for refining energy to reach the target tensile index was almost twice as high as that of the feed pulp. The thin-walled fibre fraction could be used as reinforcement pulp having properties as good as the feed pulp, but it clearly needed lower specific refining energy. Sheet properties of the short fibre fractions were quite similar to those of the birch pulp, so short fibre fractions could be used to replace or blended with birch fibres. (Fig. 35).

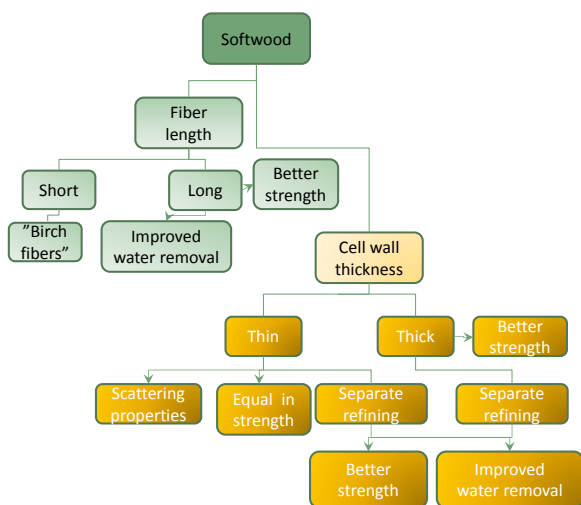


Figure 35. Utilisation of softwood kraft pulp fractions.

Blend sheet trials with TMP and GW showed that when the various chemical pulps were refined to a given tensile index, the thick-walled and the long fibre fractions gave, in the mixture with GW substantially higher freeness than the unfractionated reference pulp. The greatest differences, as regards to strength properties, were seen in the tear index of the blend sheets. The thick-walled fibre fraction clearly gave higher tear index values than the feed pulp in the mixture both with GW and TMP. Also, the long fibre fraction gave somewhat higher tear index values, especially when mixed with GW. A fractionation of the chemical pulp according to cell wall thickness did not show any positive effect on the fracture toughness index of the pulp mixture.

Separately refined fibre fractions in all cases gave higher freeness and higher fibre length of the chemical pulp-GW mixture than the unfractionated reference pulp-GW mixture. It was possible to increase the tear index with up to 16% and the fracture toughness index by up to 23% of the GW blend sheets by separate refining of the kraft pulp fractions. From the results it can be concluded that, when the kraft proportion was low (25%), refining of the thick walled fibre fraction with higher energy input gave similar or even better properties than those obtained when refined with a lower energy input. When the kraft proportion was higher, 45%, it was better to refine the thick-walled fibre fraction with a lower energy input.

6.5.2 Hardwood

Fines removal before the DEDeD bleaching resulted in a 6% lower chlorine dioxide consumption. In addition, the brightness stability was shown to be better when the fines were removed before bleaching.

If the fines fraction is removed from the birch pulp before bleaching, it could be bleached separately to reduce the content of some of the extractives components. Using a ZeQP sequence, the extractives content of the fines fraction was reduced by 40%. However, the amount of extractives remained unaffected when using the QQP sequence. Hydrogen peroxide was more effective in brightening the fines fraction than ozone. The problem in the bleaching of fines is that some of the extractives components such as betulinol cannot be removed by bleaching.

Fines could be used as a bonding agent, unbleached or bleached, in various fibre furnishes. The high bonding ability of the birch fine fraction makes it possible to use a coarser mechanical pulp in the board middle layer, which would increase the bending stiffness of the whole structure. The bonding ability of the fine fraction could be increased by refining. (Fig. 36.)

In addition to their use as a bonding material, birch fines could also be used in a biorefinery concept as a source of xylan, fatty acids, sterols and betulinol. (Fig. 36.)

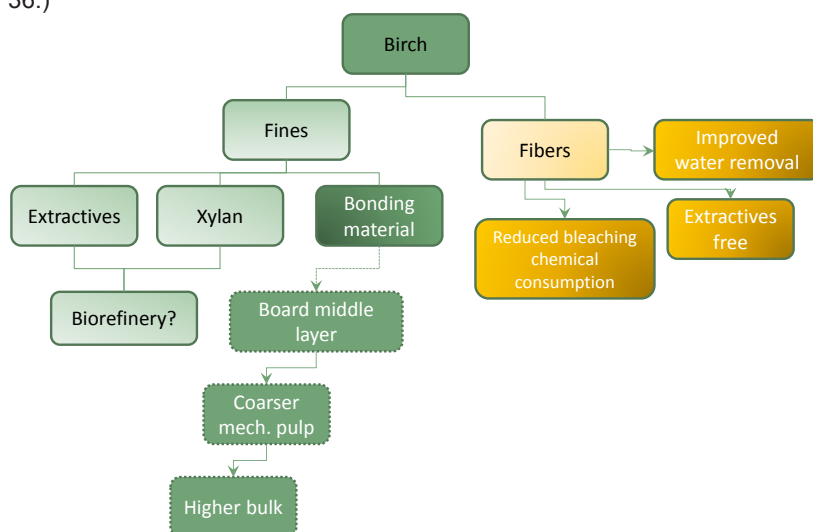


Figure 36. Utilisation of birch kraft pulp fractions.

In an industrial setup, the fines separation would probably consist of pressure screens equipped with small aperture size hole-screen, or with rotating units with augmented action, e.g. VarioSplit, Fig. 37 (Hinck and Wallendahl 1999).

VarioSplit VA1E

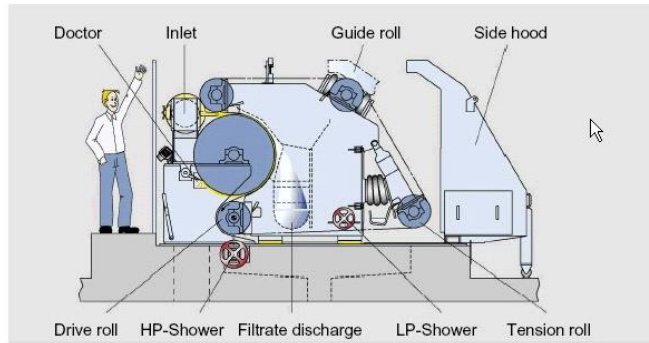


Figure 37. Equipment for removing of fines and thickening of pulp suspension (Hinck and Wallendahl 1999).

The hydrocyclone coarse fraction had a slightly better tensile stiffness index at a given SR number than the birch feed pulp, and as a result it should be optimal for fine paper and board top layer. In addition, the coarse fraction presumably would have better dewatering properties than the unfractionated birch pulp, at least at the wire section, because fines were removed (Fig. 36).

Vessel-picking tendency of eucalyptus pulp (Fig. 38) was significantly reduced by removing vessel elements from the pulp and also by refining the vessel-rich fraction. However, the separation of the vessel-elements from eucalyptus pulp is not cost-effective with the hydrocyclones, because in order to be effective enough for the vessel separation, the hydrocycloning should be carried out in several stages using low consistencies.

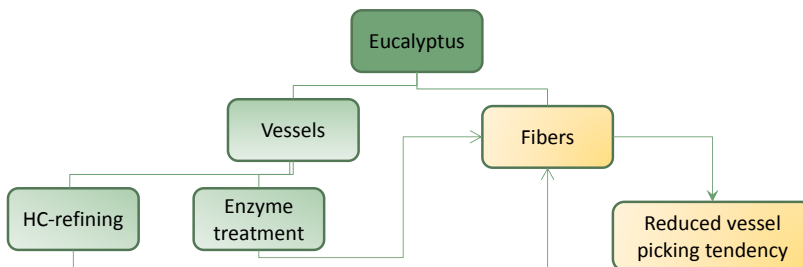


Figure 38. Treatment of eucalyptus kraft pulp fractions.

7. Conclusions and recommendations

The aim of this thesis was to clarify applicability of fractionation of softwood and hardwood kraft pulp, and utilisation of the fractions.

The main conclusions answering the research questions listed in Chapter 1.1, Table 1 are the following:

- Applicability of fractionation before the bleaching
 - Primary fines of birch had high content of lignin, metals and extractives and removing it before the bleaching decreased the pulp chlorine dioxide consumption and improved the brightness stability of the pulp. In addition this pulp was practically extractives-free.
- Applicability of fractionation after the bleaching
 - Fractionation of bleached softwood and hardwood pulps proved to be a potential method to produce fibre fractions that had better properties than the initial pulp, and they could be further tailored to fit different end-products. Softwood kraft pulp long and thick-walled fibre fractions had better dewatering ability and high tear strength. Separately refined softwood fibre fractions gave in all cases higher freeness and higher fibre length of the chemical pulp-GW mixture than the unfractionated reference pulp-GW mixture. Due to the higher fibre length also the tear and fracture toughness index of the separately refined fibre fraction-GW mixture was higher than that of the unfractionated kraft pulp and GW mixture.
 - Through hydrocyclone fractionation of birch pulp a coarse fraction was obtained having a high tensile stiffness and no extractives. The fine fraction had a high bonding ability and a high xylan and extractives content.
 - The refining of the hydrocyclone separated vessel-rich fraction of eucalyptus pulp decreased the vessel picking tendency to the same or even lower level than that of the unfractionated eucalyptus pulp.
- Utilisation of the fibre fractions
 - Softwood long and thick-walled fibre fractions could be used in products that need high strength, especially tear strength. Softwood thin-walled fibre fraction could fit for the same products that softwood kraft pulp is already used today. Softwood short fibre fraction could be used to replace birch fibres in paper and board products. The

birch coarse fraction obtained by hydrocycloning could be utilized in the top layer of board or in fine paper. The fine fraction obtained by hydrocycloning and screening could be exploited in board middle layer for bonding making it possible to use coarser mechanical pulp. One possible application for the birch fines could be addition of them in the softwood kraft cooking. In softwood kraft cooking, there are resin acids and also a higher content of fatty acid soaps, which could facilitate carrying the remaining pitch to the pulping liquor. At the same time, the xylan rich birch fines could improve the strength of the softwood pulp.

- Vessel-rich fraction of eucalyptus pulp could possibly be further converted to nanocellulose.

7.1 Limitations and future research recommendations

Although, in this thesis the utilisation of the fibre fractions is extensively presented, the techno economical feasibility of the fractionation both with hydrocyclones and screens should be analysed. In this work, the refining of the softwood pulp fractions was not optimized. This should be done in order to realize the full potential of fibre fractions.

Utilisation of birch fines could be further studied. Fines could also be used in a biorefinery concept as a source of xylan, fatty acids, sterols and betulinol. The separation of these components from birch fines could be studied more.

In order to be cost effective, the fractionation using hydrocyclones should be performed at higher consistencies. To realise this, more development work is needed in order to manufacture hydrocyclones or other separation devices that operate at a higher consistency than the current equipment does.

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PAPER I

**Effect of cell wall thickness
and fines on bleaching of
softwood kraft pulp**

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Effect of cell wall thickness and fines on bleaching of softwood kraft pulp

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SUMMARY

The effectiveness of various bleaching chemicals on softwood kraft pulp fibres of different cell-wall thickness was studied and the effect of primary fines on bleaching was investigated. Softwood kraft pulps of different average cell-wall thickness were obtained by fractionating with hydrocyclones. After the fractionation unbleached softwood kraft pulp fractions were treated with oxygen, chlorine dioxide, hydrogen peroxide and ozone. In the oxygen stage, kappa reduction increased and the consumption of sodium hydroxide per unit decrease in kappa number decreased with cell wall thickness at a given primary fines content. The consumption of hydrogen peroxide per unit decrease in kappa number increased with cell wall thickness at the same primary fines content. The consumption of chlorine dioxide and ozone per brightness unit gained decreased with cell wall thickness. In addition, the results showed that primary fines adversely affected the hydrogen peroxide bleaching of the pulp.

KEYWORD

Fractionation, hydrocyclone, cell wall thickness, primary fines, bleaching

INTRODUCTION

The cell wall thickness of softwood varies within the tree, along the stem from butt to top, and also with age. In addition the proportion of different cell wall layers varies between latewood (thick-walled

fibres) and earlywood (thin-walled fibres) (Table 1 (1)).

The differences in chemical composition between thick-walled latewood and thin-walled earlywood are due to differences in the distribution of components in the cell wall (Table 2). Thick-walled latewood fibres have a lower content of lignin due, indirectly, to the difference in cell wall thickness. At the beginning of the cell wall thickening process, the first 4-6 lamellae of the secondary wall form a 0.1-0.2 µm thick lignin-rich S1 layer (2). In temperate softwoods, the S2 layer of the secondary wall varies widely in thickness. In latewood cells, the secondary wall consists of approximately 30-40 lamellae and contains more cellulose and less lignin than the P and S1 layers. In earlywood walls, the S2 layer is considerably thinner. Hence the content of lignin is higher in thin-walled earlywood cells than in thick-walled latewood cells (2). The compound middle lamella (M+P) contains up to 0.88 g/g lignin, whereas the lignin content of the secondary cell wall of conifer tracheids ranges from 0.22 to 0.25 g/g (3).

Besides fibres, softwood pulp also contains a small amount, approximately 1 to 3 percent of the o.d. pulp, of primary fines. The primary fines consist of ray

cells, some broken fibres and thin sheets from the fibre surface (4,5). The fines fraction differs from the fibre fraction in that it has higher contents of lignin, metal ions and extractives. Fines have also been found to contain slightly more xylan and glucomannan (4). The lignin in primary fines has a high molar mass and few phenolic hydroxyl groups (5). The lignin in ray cells, the main constituent of primary fines, has more "condensed" lignin, with more aromatic carbon-carbon linkages than in other pulp fractions (6,7).

It is also known that various bleaching chemicals differ in the way they react with different lignin structures and also their location across the cell wall (8,9). The powerful oxidants, like ozone, react more rapidly with outer cell wall material, P+S1 and S3 layers, while reaction with lignin in the interior wall S2 appears to be slowed down by mass transfer limitations. According to Wang (8) hydrogen peroxide and chlorine dioxide produce uniform residual lignin distributions. However, according to Laine (10) only a small reduction in the surface lignin is obtained by hydrogen peroxide treatment. Kleen *et al.* (11) found that hydrogen peroxide removes surface lignin from kraft pulp effectively and that hydrogen peroxide cannot penetrate the fibre wall as well

Table 1.
Proportions of different cell wall layer in spruce tracheids (1).

Layer	Earlywood		Latewood	
	Thickness µm	Proportion %	Thickness µm	Proportion %
P	0.1	6	0.1	2
S1	0.2	13	0.3	7
S2	1.4	79	4.0	90
S3	0.03	2	0.04	1
Total	1.7		4.4	

Table 2.
Proportion and distribution of cellulose and lignin in earlywood and latewood of softwood (3).

Layer	Cellulose, % of total cellulose		Lignin, % of total lignin	
	Earlywood	Latewood	Earlywood	Latewood
M+P	4	3	27	18
S1	9	5	10	8
S2+S3	87	92	63	74

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as chlorine dioxide does. After oxygen delignification, the content of residual lignin in the P+S1 and S3 layers is higher than in the S2 layer (8). According to Wang (8) oxygen delignification maintains the nonuniform lignin distribution created in the pine kraft pulping, with the P+S1 and S3 layers containing about 30-35% more lignin than the S2 layer. According to Laine (10) oxygen delignification reduced the total lignin content by about 50%, while the surface lignin, originating from the remnants of the middle lamella and lignin reprecipitated during cooking, decreased only about 15%. On the other hand, Kleen *et al.* (11) found that oxygen delignification removed a higher fraction of the surface lignin (30%) than of the total lignin (20%) from the softwood kraft pulp.

The objective of this study was to investigate the overall effectiveness of various bleaching chemicals (i.e. bleaching chemical consumed per kappa number reduction and bleaching chemical consumed per brightness units gained) on softwood kraft pulp fibres of different cell-wall thickness, and to also study the effect of primary fines on bleaching.

MATERIALS AND METHODS

Raw material and fractionation

Unbleached softwood kraft pulp from a Finnish mill (66% pine, *Pinus sylvestris* and 34% Norway spruce, *Picea abies*) was fractionated using Noss Ab hydrocyclones to obtain pulps of different cell wall thickness. It is known from the literature (12) that hydrocyclone separation takes place on fibre wall thickness so, that thick-walled fibres are directed to the reject fraction and thin-walled fibres to the accept fraction. Prior to the hydrocy-

clone trials the pulp was screened to reduce its shive content. The hydrocyclone trials were carried out as a two-stage system, in which the rejects from the primary stage were fed to the secondary stage and the accepts from the secondary stage were fed back to the primary stage (Fig. 1). Five different mass reject rates (RRm) were used (19%, 27%, 45%, 72% and 91%) and the feed consistency of the primary stage was varied from 0.12 to 0.68%.

For a portion of the accepts, about 57 to 70% of the fines were removed before the bleaching trials to obtain approximately the same fines content as in the reject fractions. This permitted further investigation of the effect of fines content. Primary fines (4%) were removed using a rotating wire drum, Attisholz laboratory filter, with a 200-mesh (76 µm) wire. After the fines removal, the pulps had a fines content of 1 to 2% and kappa number was about 26.

In summary the pulps available for bleaching were as follows

- Feed
- Feed with excess fines removed: Feed'
- Thick walled pulps (rejects): Rm19r, Rm27r, Rm45r, Rm72r, Rm91r
- Thin walled pulps (accepts): Rm19a, Rm27a, Rm45a, Rm72a, Rm91a
- Thin walled pulps (accepts) with excess fines removed: Rm19a', Rm27a', Rm45a', Rm72a', Rm91a'

Bleaching

The unbleached fibre pulps: feed pulp, reject pulp, accept pulp containing all the fines and accept pulp from which fines were removed, were treated with oxygen,

chlorine dioxide, hydrogen peroxide and ozone. Oxygen delignification was performed in steel autoclave bombs with air bath heating. Ozone treatment was carried out in a plastic flow-through reactor. The chelation, chlorine dioxide, alkaline extraction and hydrogen peroxide treatments were carried out using sealed polyethylene bags in a thermostatically controlled water bath. Standard laboratory washing was carried out between stages: Pulp was diluted to 5% consistency with deionised water of the same temperature as that of the preceding stage. After dewatering, the pulp was washed twice with cold deionised water of an amount equivalent to ten times the absolutely dry pulp amount.

The bleaching chemical treatments were carried out under the following conditions:

- Chelation (Q) before oxygen and hydrogen peroxide treatments: 70 °C, 3% consistency, 60 min reaction time, EDTA 0.2% on pulp, initial pH adjusted to 4.3.
- Oxygen treatment (O): 90 °C, 8% consistency, 30 min temperature increase time, 60 min reaction time, NaOH charge (% on pulp) 0.07*incoming kappa number, 0.5% MgSO₄, oxygen pressure 8 bar. Final pH was from 10.8 to 11.6. Residual sodium hydroxide was determined by titration with hydrochloric acid.
- Chlorine dioxide treatment (D): 50 °C, 8% consistency, 60 min reaction time, active chlorine charge (% on pulp) 0.2*incoming kappa number, initial pH adjusted to ~ 3. Residual chlorine dioxide was determined by titration with sodium thiosulphate.
- Alkaline extraction (E) after chlorine dioxide and ozone treatments: 60 °C, 10% consistency, 60 min reaction time, initial pH~11.
- Hydrogen peroxide treatment (P): 90 °C, 10% consistency, 60 min reaction time, 2.0% NaOH on pulp, 0.25% MgSO₄ on pulp, 0.2% DTPA on pulp, 3.0% hydrogen peroxide on pulp. Final pH was from 9.4 to 9.6. Residual hydrogen peroxide was determined by titration with sodium thiosulphate.
- Ozone treatment (Z): 50 °C, 12.5% consistency, 0.35% ozone on pulp, initial pH adjusted to 3. The ozone formation was determined from potassium iodide solution by titration with sodium thiosulphate.

Kappa number (ISO 302), viscosity (ISO 5351) and brightness (brightness was

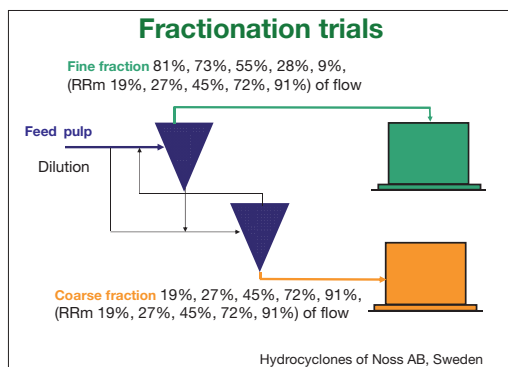


Fig. 1 Trial configuration for hydrocyclone fractionation.

measured from the split sheet, ISO 2470) were determined after the bleaching chemical treatments. In addition to routine analyses, a chemical analysis based on total solubilisation of pulp by enzymatic hydrolysis was used (13). The lignin content, the content of phenolic hydroxyl groups and the content of conjugated groups were determined from the sample solution. Fines content was determined using a Dynamic Drainage Jar (DDJ) with a wire hole diameter corresponding to a 200-mesh (76 µm) wire. Cell wall thickness measurement was performed according to Lammi (14), and Simons' staining according to Simons (15).

RESULTS AND DISCUSSION

Fibre properties

After the hydrocyclone treatment pulps of different cell wall thickness were obtained. Cell wall thickness varied from 3.9 µm to 6.2 µm (Fig. 2).

Fines accumulated during fractionation in the thin-walled accept pulp. The accumulated fines in the accept fraction had a higher lignin content and it increased the kappa number of the pulp (Fig. 3).

Despite the higher kappa numbers, the pulps having thin-walled fibres and a high fines content was brighter than the pulp having thick-walled fibres (Fig. 4) in agreement with Brännvall *et al.* (16). One reason for this is that the hand sheets made from the pulp with thin-walled fibres and high fines content contained more fibres for a given weight, and as a result this sheet had more light-reflecting surfaces and consequently had a higher

Table 3

Simons' staining.

	Cell wall thickness, µm	Yellow, %	Blue, %	Undyed, %
Feed (original pulp)	4.7	79	21	1
Thick-walled	6.2	45	54	1
Thin-walled	3.9	73	25	1

light scattering coefficient.

The structure of the thin-walled and thick-walled fibres was significantly different as indicated by Simons' staining (Table 3). Simons' staining reveals the structure of the fibre, the internal fibrillation and the looseness of the fibre wall. Simons' stain is a mixture of two dyes, which have different molecular size. Orange dye is assumed to absorb to the fibre wall if there is enough space, and if the fibre wall is denser (smaller pores) the fibre is dyed blue since the blue dye have a smaller particle size (15).

The proportion of yellow-dyed fibres

was 45% for the pulp containing thick-walled fibres, and 73% for the pulp containing thin-walled fibres (Table 3). This means that the structure of the thick-walled fibres is denser than that of the thin-walled fibres. The structure of the feed pulp was about the same as that of the pulp containing thin-walled fibres, because the average cell wall thickness of the feed pulp was closer to that of the pulp containing the thin-walled fibres. The feed pulp contained more thin-walled fibres than thick-walled fibres.

Bleaching chemical treatments

In the oxygen stage kappa reduction increased (Fig. 5a) and the consumption

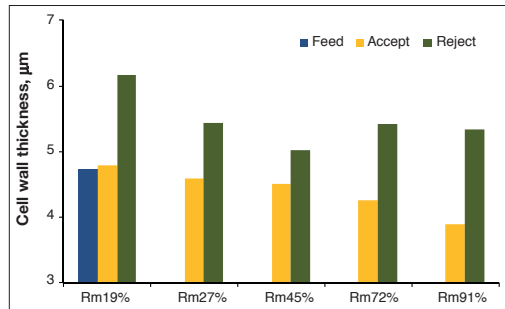


Fig. 2 Cell wall thickness of the feed (original pulp), accept (thin-walled) and reject (thick-walled) pulp for different mass reject ratios.

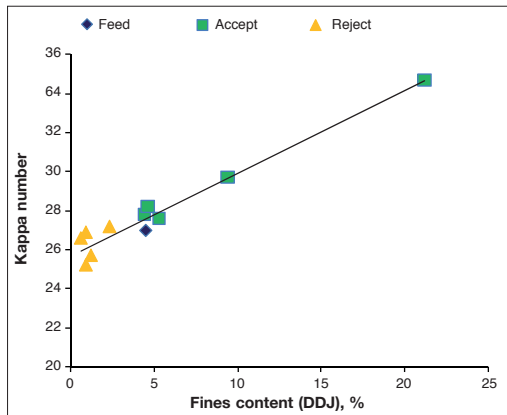


Fig. 3 Kappa number of the feed, accept and reject pulps plotted against fines content.

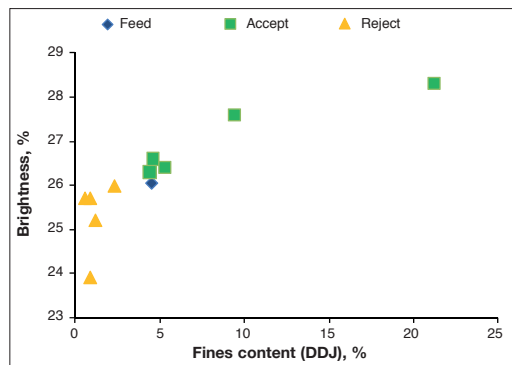


Fig. 4 Brightness of the feed, accept and reject pulps plotted against fines content.

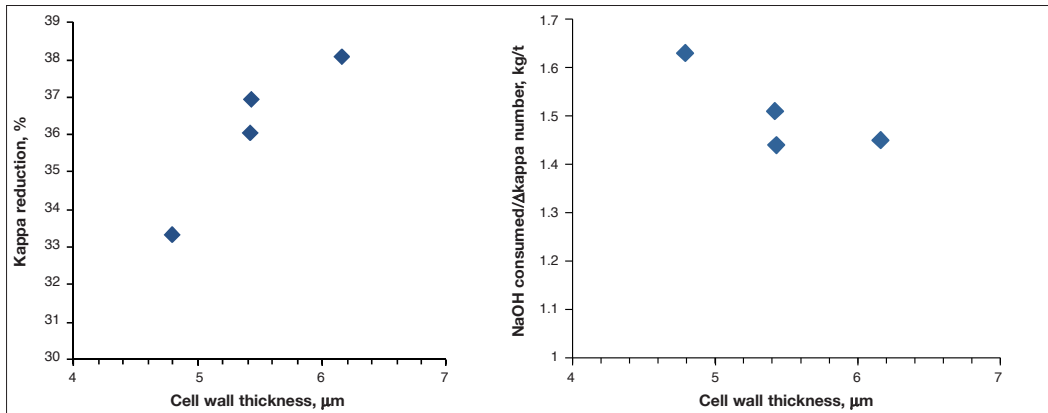


Fig. 5. a) Kappa reduction in oxygen delignification as a function of cell wall thickness. Fines content was from 1 to 1.9%. b) NaOH consumption per kappa number reduction as a function of cell wall thickness. Fines content was from 1 to 1.9%. Points in figure are for pulps: Rm19a', Rm19r, Rm27r, Rm72r.

of sodium hydroxide per unit decrease in kappa number decreased (Fig. 5b) with the cell wall thickness at a given fines content. One possible explanation for these findings is that the proportion of S2 layer is greater in thick-walled fibres than in thin-walled fibres (1).

According to the literature, the dissolution of lignin by oxygen is more effective from the S2 layer than from the (P+S1) or S3 layers (8,10). It is known that oxygen predominantly reacts with lignin structures containing a free phenolic hydroxyl group. The concentration of phenolic

hydroxyl groups in the lignin of the secondary wall of the fibres is more than double that found in the middle lamella and primary wall lignin (6). The pulp with thick-walled fibres contained more phenolic groups, which were formed during the cooking (Fig. 6). After the oxygen treatment, the number of phenolic groups was lower in the pulp containing thick-walled fibres than in the pulp containing thin-walled fibres. This indicates that the phenolic groups are possibly more stable in pulp containing thin-walled fibres. There may also be differences in how

they are morphologically located, i.e. differences in accessibility, phenolic groups in thick-walled fibres being more accessible than those in thin-walled fibres. Correlation between the sodium hydroxide consumption and fines content of the pulp was not found. It is known that the lignin in primary fines has a high molar mass and few phenolic hydroxyl groups, which could explain the poor reactivity of the pulp with high fines content towards oxygen (5).

No correlation was found between the cell wall thickness and the chlorine dioxide consumption per unit decrease in kappa number after the chlorine dioxide treatment. A small correlation was seen

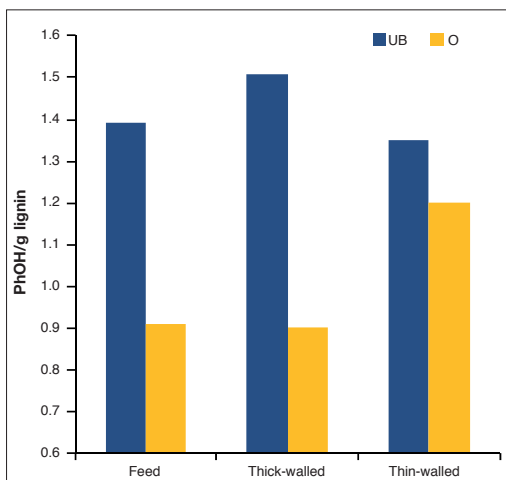


Fig. 6 Concentration of phenolic groups in unbleached and oxygen-treated pulps. UB – unbleached, O – oxygen delignified. Cell wall thicknesses: Feed 4.7 μm, Thick-walled 6.2 μm, Thin-walled 3.9 μm.

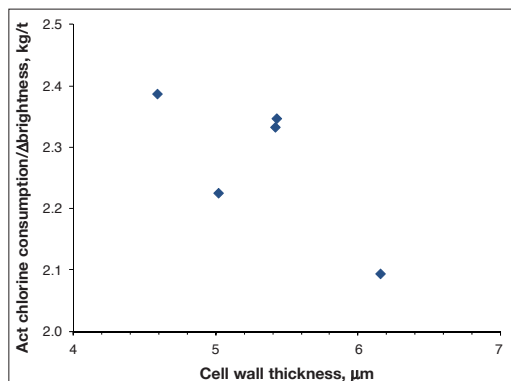


Fig. 7 Active chlorine consumption kg/Δ brightness as a function of cell wall thickness. Brightness was measured after alkaline extraction stage. Fines content was from 1 to 1.7%. Points in Figure are for pulps: Rm19r, Rm27a', Rm27r, Rm45r, Rm72r.

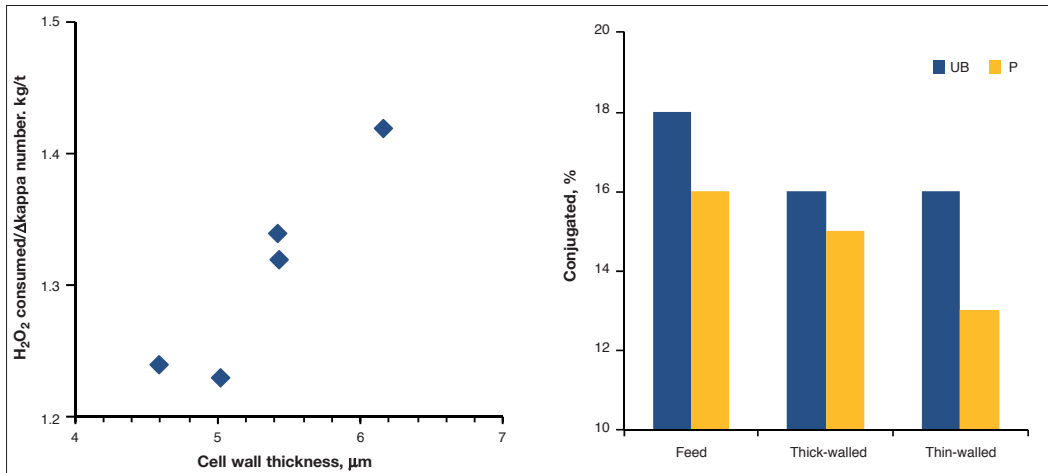


Fig. 8. a) Hydrogen peroxide consumption / Δ kappa number as a function of cell wall thickness. Fines content was from 1 to 1.7%. Points in Figure are for following pulps: Rm19r, Rm27a', Rm27r, Rm45r, Rm72r. b) Amount of conjugated groups in unbleached and hydrogen peroxide-treated pulps. Pulp was chelated before hydrogen peroxide treatment. Cell wall thicknesses: Feed 4.7 μm, Thick-walled 6.2 μm, Thin-walled 3.9 μm.

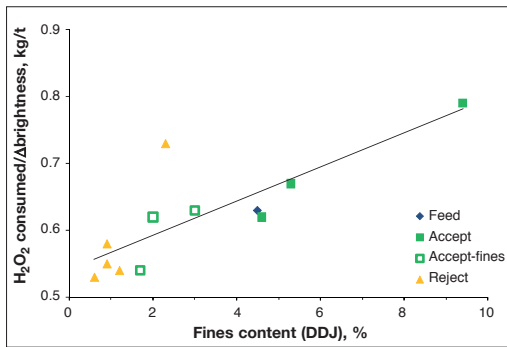


Fig. 9. Consumption of hydrogen peroxide as a function of primary fines content.

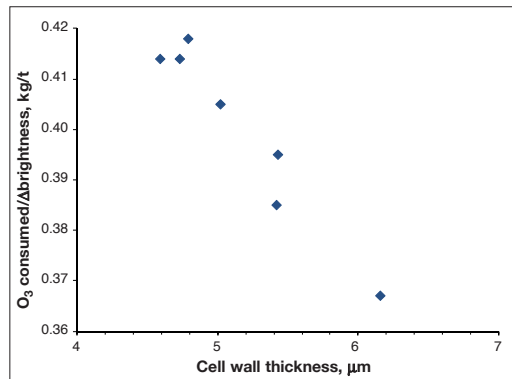


Fig. 10 Ozone consumption/Δ brightness as a function of cell wall thickness. Brightness was measured after alkaline extraction stage. Fines content was from 1 to 1.9%. Points in Figure are for following pulps: Feed', Rm19a', Rm19r, Rm27a', Rm27r, Rm45r, Rm72r.

between the cell wall thickness and the chlorine dioxide consumption per brightness unit gained (Fig. 7), the latter decreasing with cell wall thickness. Laine *et al.* (10) found surface lignin played a significant role with regard to brightness development during bleaching. They suggested that surface lignin is very probably more coloured than lignin in the other regions of the fibres. Also, Abe (17) found that a prebeating, i.e. removal of surface lignin, improved bleachability of unbleached kraft pulp. Thin-walled fibres probably contain more lignin characteristic of surface lignin i.e. middle lamella lignin and precipitated lignin and this explains their poorer bleachability with chlorine dioxide. In addition, both Laine

et al. (10) and Kleen *et al.* (11) found that chlorine dioxide does not remove surface lignin effectively.

Consumption of hydrogen peroxide per unit decrease in kappa number increased with cell wall thickness at the same fines content (Fig. 8a). In addition, the number of conjugated groups, containing a carbonyl group, was reduced more by hydrogen peroxide treatment of the pulp containing thin-walled fibres than of the pulp containing thick-walled fibres (Fig. 8b).

This also indicates that the hydrogen

peroxide treatment was more effective on the pulp with thin-walled fibres. Thinner fibres have a higher fraction of the lignin on the surface; and the increased removal of conjugated structures from thinner fibres seems to be because the surface lignin is more accessible. Kleen *et al.* (11) also found that peroxide cannot penetrate the fibre wall as well as chlorine dioxide and that hydrogen peroxide removes surface lignin effectively.

The consumption of hydrogen peroxide per brightness unit gained increased with increasing fines content (Fig. 9),

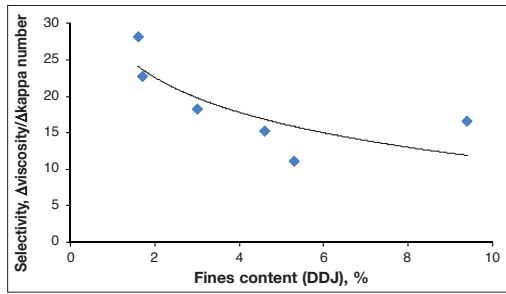


Fig 11. Selectivity (Δ viscosity/ Δ kappa number) in ZE stage plotted against fines content of the pulp.

while metal content of the pulps was about the same. This might be caused by the differences in lignin content and structure (18). According to Bäckström *et al.* (18) the better brightness gain achieved with no primary fines is due to the removal of chromophores.

The ozone consumption per brightness unit gained decreased with cell wall thickness (Fig. 10). The (P+S1) and S3 layers are said to react more quickly with ozone than the S2 layer (8). In the thin-walled fibres the proportions of (P+S1) and S3 layers are greater (1) and probably as a result of this the consumption of ozone was higher in the pulp containing thin-walled fibres.

The fines content seemed to have a slight influence on the selectivity (Δ viscosity/ Δ kappa number) values after the ozone treatment, so that the pulp containing a high amount of fines had a better selectivity (Fig 11.). The fines might have preserved the fibres, because, as mentioned earlier, ozone reacts more rapidly with outer cell wall material, (P+S1) and S3 layers, while reaction with lignin in the interior wall S2 appear to be slowed down by mass transfer limitations (8).

CONCLUSIONS

The results showed that the morphological features of the fibres influence the bleaching of the pulp. Results support earlier hypotheses that oxygen predominantly reacts with lignin in S2 layer, because the kappa reduction in the oxygen stage increased with the cell wall thickness. No correlation was found

between the cell wall thickness and the chlorine dioxide consumption per unit decrease in kappa number. However, the consumption of chlorine dioxide per brightness unit gained decreased with the cell wall thickness. In the hydrogen peroxide stage the bleachability of the pulp deteriorated due to the primary fines. The consumption of hydrogen peroxide per unit decrease in kappa number increased with the cell wall thickness. Ozone as a powerful oxidant reacted preferably with the surface lignin. This was seen in the higher consumption of ozone per brightness unit gained in the case of the pulp containing thin-walled fibres.

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PAPER II

**Effect of birch kraft pulp
primary fines on bleaching and
sheet properties**

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EFFECT OF BIRCH KRAFT PULP PRIMARY FINES ON BLEACHING AND SHEET PROPERTIES

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By removing the primary fines from an oxygen-delignified mill birch pulp, a fiber fraction was obtained having low metals content and no extractives. After DEDeD bleaching the fiber fraction had somewhat higher brightness and better brightness stability than the birch pulp containing the primary fines. The fines fraction was enriched with lignin, extractives, xylan, and metals. Bleaching the fines fraction in a QQP sequence did not affect the extractives, whereas a ZeQP sequence clearly reduced the extractives content. In a biorefinery concept, the fines fraction could be utilized as a source of xylan, fatty acids, sterols, and betulinol. Another possibility is to use the fines fraction unbleached or separately bleached as a bonding material in various fiber furnishes.

Keywords: *Betula; Kraft pulp; Fines; Ozone bleaching; Hydrogen peroxide; Chlorine dioxide; Metal ion; Bonding; Brightness stability; Extractive content*

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INTRODUCTION

The use of fractionation techniques is increasing in the pulp and paper industry. One reason is the possibility to remove and separately treat fiber fractions that may contribute negatively to pulp and papermaking. For example, by removing the primary fines before bleaching, closure of the bleaching loop at the pulp mill may be facilitated, since the metals ion content is reduced before bleaching. In papermaking, problems related to stickies, smell and odor caused by extractives could be avoided by removal of the primary fines, since most of the extractives are found in primary fines. If the primary fines are treated separately, and the extractives and metal ions content can be reduced, then the primary fines can be utilized in papermaking.

Primary fines consist of ray cells, some broken fibers, and thin sheets from the fiber surface. Primary fines usually represent between 1 and 3 percent of the o.d. mass of pulp, depending on the wood species. The fines fraction differs from the fiber fraction in that it has higher contents of lignin, metal ions, and extractives (Bäcström and Brännvall 1999; Liitiä et al. 2001; Hinck and Wallendahl 1999; Treimanis et al. 2009; Treimanis 2009).

In birch the majority of the extractives are located inside the parenchyma cells. Birch pulp extractives cause severe problems in pulp and papermaking. Of the birch extractives, betulinol is usually the main component in precipitations or stickies found in both pulp and paper mills. Its melting point is 261 °C; thus it is crystalline through the all stages of the pulp making. Sitosterol can be oxidized to a form that results in a bad smell;

sitostanol is again saturated and stable. Both are found in stickies, although they are not sticky themselves (Holmbom 2003; Back and Allen 2000). Fatty acids are sticky, especially saturated fatty acids in the form of metal soaps, and they have been found to impair the degree of sizing (Lidén and Tollander 2004). Both the fatty acids and sitosterol components can be oxidized, which can result in taste and odor problems. Especially, the unsaturated fatty acids are easily oxidized, leading to volatile bad smelling aldehydes, such as hexanal and nonal (Oyaas 2000). All lipophilic substances, which are enriched on the fiber surfaces, tend to decrease the fiber-fiber bonding ability (Kokkonen et al. 2002).

The objective of the study was to clarify the changes in chemical composition of the pulp by removal of the primary fines from an oxygen-delignified mill birch kraft pulp before bleaching, and how the bleaching chemical consumption and pulp properties are affected using a DEDeD sequence. Also the effects of separate bleaching of the fines fraction using QQP and ZeQP sequences were investigated, especially in order to reduce the extractives content. Finally, the possibilities of utilizing the fines fraction, unbleached or bleached, as a bonding agent for, e.g., chemimechanical pulp, were evaluated.

EXPERIMENTAL

Primary fines (4%) were removed from an oxygen-delignified mill birch kraft pulp (before refining) using KCL's Super DDJ (Dynamic Drainage Jar) equipment, which is composed of a tank with a 200-mesh wire and a mixer. This separation method was chosen since it is easy way in the laboratory scale to separate fibers and fines. In an industrial setup the fines separation would probably consist of pressure screens equipped with small aperture size hole-screen, or with rotating units with augmented action, e.g. VarioSplit (Hinck and Wallendahl 1999).

In this paper the original birch pulp containing primary fines will be called birch pulp, primary fines-free birch pulp will be called fiber fraction, and birch primary fines will be called fines fraction.

Bleaching

The birch pulp and the fiber fraction were bleached in the laboratory using a DEDeD sequence. Bleaching experiments were performed in a sealed plastic jar. The brightness target for the pulps was 88% ISO. The bleaching conditions are shown in Table 1.

The fines fraction was bleached using QQP and ZeQP sequences. Hydrogen peroxide and ozone were charged in such a way that both the sequences had about the same bleaching chemical consumption calculated as OXE (oxidizing equivalents), 1780 OXE/kg. The conditions were as follows:

- Chelation (Q): 70°C, 2 % consistency, 20-30 min, EDTA 0.4-0.5% calculated on dry pulp, initial pH ca. 4.0.
- Hydrogen peroxide stage (P) in QQP sequence: 80°C, 15% consistency, 180 min, NaOH 2%, MgSO₄ 0.1%, H₂O₂ 4% calculated on dry pulp.
- Ozone stage (Z) in ZeQP sequence: approx. 50°C, 1.4% consistency, initial pH ca. 6.

- P-stage: NaOH 0.88%, H₂O₂ 1%, other conditions the same as in QQP.
- e-stage (neutralizing washing stage) in ZeQP sequence: 70°C, 2 % consistency, 10 min, initial pH 7.5-8.0.

Table 1. Bleaching Conditions for the DEDeD sequence

Stage	D0	E1	D1	e*	D2
Consistency, %	9	10	9	3	9
Temperature, °C	50	65	65		70
Reaction time, min	60	60	120	2	180
Final pH	<2.5	10.5-11.0	~4	~9-9.5	~4.5
ClO ₂ charge, %	0.2 times incoming kappa number	-			According to the brightness after the D1
NaOH charge, %	-	0.4*ClO ₂ charge in D0	0.085*ClO ₂ charge in D1	0.4	-

* e-stage, i.e. neutralizing washing stage was performed straight away after the D1-stage.

Analysis Methods

The following analyses were conducted on the birch pulp, fiber fraction and fines fraction:

- Total residual lignin, gravimetric and acid soluble lignin. (KCL internal method TAPPI T222 modif.).
- Uronic acids were measured using an enzymatic hydrolysis followed by HPLC measurement (Tenkanen et al. 1995; Hausalo 1995).
- Acetone extracts (SCAN-CM 49).
- Wood extractives– free fatty acids, resin acids, lignans, sterols, steryl esters and triglycerides. Pulp sample was freeze-dried and extracted with acetone. The silyl derivative of the wood extractives was analyzed using gas chromatograph with flame ionization detector (GC-FID). The amounts of free fatty acids, resin acids, lignans, sterols, steryl esters, and triglycerides were determined as group sums.
- Carbohydrate composition (TAPPI T249, modif.).
- Polysaccharide composition (Janson 1974).
- Carboxyl group content was determined with the method based on magnesium ion exchange. In principle, the bound magnesium ions are eluted and determined by quantitative analysis.
- Carbonyl group content was determined according to the oxime method. The carbonyl content is related to the nitrogen content as determined by Kjeldahl procedure or elemental analysis.
- Metal content was measured using Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-AES). The samples were dissolved in nitric acid in a microwave oven before the analysis.
- Fines content using a Dynamic Drainage Jar (DDJ) equipped with a 200-mesh (76 µm) wire. Conducted on the birch pulp and the fiber fraction.

- Acetone soluble matter (SCAN-CM 49:03), uronic acid composition (Tenkanen et al. 1995, Hausalo 1995), metal ion content and post color (PC)-number (80°C, 65% RH, 48h according to ISO 5630-3 by UV-Vis reflectance spectroscopy, KCL Internal method, described in (Liitiä et al. 2004) was determined for DEDeD bleached birch pulp and fiber fraction.

RESULTS

Contents of Organic Compounds in the Birch Pulp, Fiber, and Fines Fractions

The fiber fraction and birch pulp had higher cellulose content than the fines fraction, and the fiber fraction was extractives-free (Table 2). The fines fraction had a substantially higher content of lignin, xylan, extractives, metals, and also hexenuronic acid. Also, the content of carbonyl and carboxyl groups was higher in the fines fraction. Higher content of xylan, lignin, and carbonyl groups has also been reported earlier in the fines (Treimanis 2009; Treimanis et al. 2009; Bäckström and Brännvall 1999; Liitiä et al. 2001; Hinck and Wallendahl 1999; Heijnesson-Hulten et al. 1997; Westermarck and Capretti 1988). Ray cells are known to be a main source of extractives, and that is the reason for the higher content of extractives in the fines fraction (Heijnesson-Hulten et al. 1997).

Table 2. Chemical Composition of Birch Pulp, Fiber Fraction, and Fines

	Birch pulp	Fiber fraction	Fines fraction
Cellulose, %	71.7	73.8	43.4
Lignin, %			
Gravimetric	<2.0	<2.0	5.6
Soluble	0.6	0.5	0.6
Total			6.2
Xylan, %	26.1	24.6	48.3
Uronic acid composition			
Methyl glucuronic acid, mmol/kg	31	27	27
Hexenuronic acid, mmol/kg	78	69	91
Acetone extract, %	0.31	<0.05	1.55
Carbonyl groups, mmol/100 g	1.6	1.6	3.2
Carboxyl groups, mmol/kg	153.7	148.8	218.2

The fines fraction had a clearly higher content of various extractives components than the birch pulp or the fiber fraction (Table 3). Also, the content of the various extractives components of the fiber fraction, containing in practice no fines (0.4% of DDJ fines), was substantially lower than that of the birch pulp containing 4.6% of DDJ fines. In particular, the content of harmful betulinol, a main component in deposits or stickies found at both pulp and paper mills, was substantially lower in the fines-free fiber fraction.

Also, the contents of fatty acids and sterols were substantially lower, when the fines were removed.

Table 3. Extractives Content of the Birch Pulp, Fiber Fraction, and Fines Fraction, Analyzed from Freeze-Dried Pulps

mg/kg	Birch pulp	Fiber fraction	Fines fraction
Fatty acids	170	26	1100
Betulinol	72	8	460
Lignan	39	10	540
Sterols	190	38	3000
Sterylesters	1200	310	25000
Triglyserides	72	42	760
Total	1700	430	31000

Metal Ion Contents of the Pulps

The fines fraction had a clearly higher metal content than the birch pulp and the fiber fraction (Table 4). A high metal ion content of the fines fraction has also been revealed earlier (Westermarck and Capretti 1988; Treimanis 2009). As expected, the fiber fraction had a lower content of metal ions than the birch pulp.

Table 4. Metal Ion Content

mg/kg	Birch pulp	Fiber fraction	Fines fraction
Copper	<0.5	<0.5	5.3
Iron	<3	<3	100
Magnesium	150	140	250
Manganese	100	69	350
Silica	65	42	220
Calcium	1500	1200	3700

Particularly, the content of manganese, silica and calcium was lower in the fiber fraction than in the birch pulp. However, the positive thing was that the content of magnesium, a protector in hydrogen peroxide bleaching, was not much lower in the fiber fraction than in the original birch pulp.

Effect of Fines Removal on the DEDeD Bleaching Efficiency

Higher final brightness at 6% lower active chlorine consumption was obtained for the fines-free fiber fraction compared to the birch pulp. Calculated as active chlorine consumption per kappa unit reduction or brightness unit increase, there were no differences between the pulps, i.e. no difference in bleachability (Table 5).

A slight difference was seen in the brightness stability of the birch pulp and that of the fiber fraction. Brightness values before the aging treatment was about the same for both pulps (Table 6). However, after the aging treatment the birch pulp had a somewhat lower brightness value than the fiber fraction.

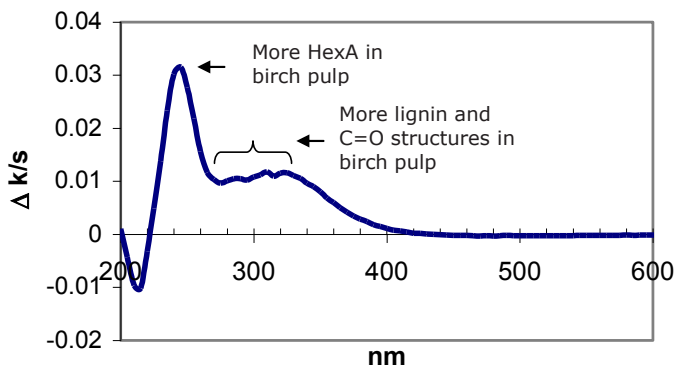
Table 5. Kappa Number and Brightness of the Bleached Pulps and Bleaching Chemical Consumption

	Birch pulp	Fiber fraction
Final kappa number	1.0	0.88
Final brightness, %	88.2	88.6
Active chlorine consumption, kg/BDt	46.37	43.60
Active chlorine consumption/ Δ kappa number, kg/BDt	3.93	3.96
Active chlorine consumption/ Δ brightness, kg/BDt	1.07	1.09

Table 6. Brightness Before and After the Aging Treatment, and PC Number (465nm) for 48h, 80°C, 65% Relative Humidity

	Birch pulp	Fiber fraction
Brightness before treatment, %	88.61	88.46
Brightness after treatment, %	75.81	76.50
PC (Post Color) number	3.13	2.86

The PC number was affected by the content of lignin, hemicellulose component/uronic acids, extractives, and also the metal ions. The birch pulp had higher extractives content, and also higher hexenuronic acid content (although below the determination limit) than the fiber fraction. Also the UV-Vis spectra revealed that the fiber fraction had a lower content of hexenuronic acids and lignin, and also less C=O structures than the birch pulp (Fig. 1).

**Fig. 1.** Difference between the UV-Vis spectra of the birch pulp and the fiber fraction

Effect of the QQP and ZeQP Bleaching of the Fines Fraction on the Extractives

The hydrogen peroxide, QQP bleaching, was unable to remove the extractives from the birch fines fraction although it acts also as an alkaline extraction stage (Table 7).

It is known that the problems with birch extractives have anatomical and chemical explanations (Back and Allen 2000; Sjöström 1981, Laamanen 1984). In birch the majority of the extractives are located inside the parenchyma cells, which have rather small pits. This renders the birch pulp extractives more troublesome than in other hardwoods.

Table 7. Extractives Content of the Fines Fraction and QQP Bleached Fines Fraction

mg/kg	Fines fraction	QQP bleached fines fraction
Fatty acids	1100	2200
Betulinol	460	520
Lignan	540	680
Sterols	3000	3000
Sterylesters	25000	25000
Triglycerides	760	790
Total	31000	32000

Similar to what was earlier found by Laamanen (1984), hydrogen peroxide treatment of birch kraft pulp in the laboratory, with a large dose of 5%, did not change the composition of the extractives. The reason for this was said to be that hydrogen peroxide was unable to penetrate into the (extractives) parenchyma cells. Furthermore, in the alkaline hydrogen peroxide stage, in which there are significant concentrations of Ca^{2+} - and Mg^{2+} - ions, the fatty acids will form metal soaps rather than soluble fatty acids soaps, and due to this the extractives content will not decrease (Fernando and Daniel 2005). In addition, it has been observed that the sterols remaining in bleached pulps are present almost exclusively inside the parenchyma cells (Fernando and Daniel 2005). It is also mentioned in the literature (Fernando and Daniel 2005) that betulinol and saturated fatty acids are very resistant towards oxidation.

The total content of extractives was decreased by ZeQP bleaching from 31000 mg/kg to 19000 mg/kg (Table 8). The extractives content of the fines fraction was about 42% lower after the Ze bleaching than that of the unbleached fines fraction, and after the ZeQP sequence about 40% lower. However, the content of some extractives components after the hydrogen peroxide stage in ZeQP bleaching was about the same or even greater than in the unbleached fines due to the same reasons as in the case of the QQP bleaching.

Table 8. Extractives Content of the Unbleached Fines Fraction, the Fines Fraction after Ze-stage, and the ZeQP Bleached Fines Fraction

mg/kg	Unbleached fines fraction	Fines fraction after Ze	ZeQP bleached fines fraction
Fatty acids	1100	1100	2000
Betulinol	460	370	400
Lignan	540	450	660
Sterols	3000	2200	2500
Sterylesters	25000	13000	13000
Triglycerides	760	760	770
Total	31000	18000	19000

The content of sterylesters was substantially lower after the bleaching than before that. The content of sterols was slightly lower in ZeQP bleached fines than in the unbleached fines. Barbosa et al. (2008) also found ozone to be effective in removal sterols in the bleaching of Eucalyptus kraft pulp.

As in the QQP bleaching of the fines fraction, the content of betulinol, lignan and triglycerides did not either change as a consequence of the ZeQP bleaching.

Birch Pulp Compared to Fines-Free Fiber Fraction

There were no big differences in the sheet properties of the DEDeD bleached birch pulp and fines-free fiber fraction (Table 9).

The light absorption coefficient of the fiber fraction was lower than that of the birch pulp. This was due to the lower lignin content of the fiber fraction than that of the birch pulp. Tensile index and Scott bond of the unrefined birch pulp were higher than those of the unrefined fiber fraction due to the higher fines content of the birch pulp. However, this means that the fiber fraction could be refined to a higher tensile index and Scott bond at a given freeness or SR number.

Table 9. Birch Pulp vs. Fiber Fraction

	Birch pulp	Fiber fraction
Bulk, cm ³ /g	1.45	1.48
Air resistance, Gurley, s	1.4	0.8
ISO brightness, %	87.3	87.9
Light scattering coefficient, m ² /kg	31.6	32.1
Tensile index, Nm/g	37.0	32.8
Scott bond, J/m ²	204	157

Utilization of the Birch Fines Fraction

A prerequisite for an industrial realization of removal of the fines fraction from the bleached kraft pulp is to find technically and economically feasible utilization possibilities. One option is to use the fines fraction, either unbleached or separately bleached, as a bonding agent in various fiber furnishes. Good results of using bleached birch fines as a bonding material in paperboard's middle layer has been obtained (Panula-Ontto and Fuhrmann 2007). In this study the possibility to mix the unbleached fines fraction or the QQP and ZeQP bleached fines with a softwood CTMP mill pulp was investigated (Table 10).

The unbleached fines fraction reduced the brightness of the CTMP blend sheet. This was due to the higher light absorption coefficient of the unbleached lignin rich primary fines. Higher bonding ability of fines fractions gave rise to increased tensile index and Scott bond of the CTMP blend sheet. Birch fines settled in the voids of the fiber network, which can be seen as clearly increased air resistance value and lower bulk of the CTMP blend sheet (Table 10).

Both the bleached fines fractions did not affect negatively the brightness of the CTMP. The brightness was even slightly improved in the case of QQP pulp. Hydrogen peroxide is effective bleaching agent in removing of chromophores, which was also seen as lower light absorption coefficient of QQP bleached fines compared to that of ZeQP bleached fines (Table 10).

Birch fines fraction, unbleached or bleached, can be used to increase Scott bond and tensile index values of CTMP-based paper. However, as expected, the bulk was decreased. The additions of the fines fraction were quite high, 10% and 20%, in this study. Lower amounts may be very well added without a negative effect on bulk. Alternatively, coarser mechanical pulp could be used, resulting in an increase of bulk but with still an acceptable bonding.

In addition to their use as a bonding material, birch fines could also be used in a biorefinery concept as a source of xylan, fatty acids, sterols, and betulinol. One possible application could be the adding of birch fines in the softwood kraft cooking. In softwood kraft cooking there is resin acids and also higher content of fatty acid soaps, which could facilitate the carrying the remaining pitch to the pulping liquor. At the same time, the xylan-rich birch fines could improve the strength (tensile stiffness) of the softwood pulp.

Table 10. Sheet Properties of CTMP + Birch Fines

	CTMP	CTMP:unbleached fines		CTMP:QQP fines		CTMP:ZeQP fines	
		90:10	80:20	90:10	80:20	90:10	80:20
Furnish composition, %	100	90:10	80:20	90:10	80:20	90:10	80:20
Bulk, cm ³ /g	2.80	2.58	2.22	2.47	2.22	2.59	2.40
Air resistance, Gurley, s	2.8	7.7	22.2	7.3	17	5.5	13
ISO brightness, %	68.5	64.5	60.5	69.1	69.7	68.5	68.6
Light absorption coefficient, m ² /kg	0.61	1.18	1.85	0.61	0.62	0.68	0.72
Tensile index, Nm/g	22.5	26.8	31.0	25.0	28.3	24.7	27.4
Standard deviation, Nm/g	0.8	1.2	0.9	1.3	1.1	0.9	0.6
Scott bond, J/m ²	67	98	121	85	112	85	103
Standard deviation, J/m ²	10	2	5	5	15	5	12

CONCLUSIONS

- By removing 4% of the fines from a birch mill kraft pulp it was possible to obtain:
- An extractives-free pulp (<0.05% acetone extractives) with low metals ion content.
 - A higher final brightness at 6% lower active chlorine consumption in DEDeD bleaching.
 - Improved brightness stability after DEDeD bleaching.

RECOMMENDATIONS

- Fines fraction could be used
- As a bonding agent, unbleached or bleached, in various fiber furnishes.
 - In a biorefinery concept as a source of e.g. xylan, fatty acids, sterols, betulinol.
- Fines fraction could be bleached
- To reduce the content of some of the extractives components. Using a ZeQP sequence, the extractives content of the fines fraction was reduced by 40%. However, the amount of extractives remained unaffected when using the QQP sequence. Hydrogen peroxide was more effective in brightening the fines fraction than ozone.
 - But the problem is that some of the extractives components like betulinol cannot be removed by bleaching.

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PAPER III

**Reinforcing ability of
fractionated softwood
kraft pulp fibres**

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PAPER IV

Birch pulp fractions for fine paper and board

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PAPER V

Evaluation of vessel picking tendency in printing

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Avaliação da tendência ao arrancamento de vasos na impressão

Evaluation of vessel picking tendency in printing

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Palavras-chave: Arrancamento de vasos, composição química, fracionamento, morfologia das fibras, refinação

Keywords: Chemical composition, fiber morphology, fractionation, refining, vessel picking

RESUMO

As celuloses industriais kraft branqueadas de eucalipto - *Eucalyptus globulus* e *Eucalyptus grandis* - foram fracionadas mediante um hidrociclone (Bauer 3") a fim de enriquecer os elementos de vasos em uma das frações. A tendência ao arrancamento de vasos foi analisada mediante método desenvolvido no KCL (Instituto Finlandês de Pesquisas de Celulose e Papel). Nesse método, folhas manuais são impressas em impressora offset plana de 4 cores, em escala natural, com tinta de impressão comercial. O teste de impressão de arrancamento de vasos foi feito para celuloses kraft de eucalipto não-fracionadas, frações ricas em vasos e pobres em vasos. As partículas arrancadas foram analisadas e contadas por meio de analisador de imagens. O teste de impressão de arrancamento de vasos também foi realizado nas frações ricas em vasos após processo de refinação em moinho PFI, nível de 2000 revoluções. O hidrociclone separou eficientemente os vasos segundo seu tamanho e formato. A análise por microscopia mostrou que os vasos da fração rica em vasos eram maiores e apresentavam uma forma mais quadrada do que os da celulose pobre em vasos. A refinação da fração rica em vasos reduziu a tendência ao arrancamento de vasos ao mesmo nível ou até a nível inferior àquele da celulose não-fracionada.

ABSTRACT

Bleached eucalyptus kraft mill pulps - Eucalyptus globulus and Eucalyptus grandis -, were fractionated using hydrocyclone (Bauer 3") in order to enrich the vessel elements in one of the fractions. The vessel picking tendency was analyzed with a method developed at the Finnish Pulp and Paper Research Institute (KCL). In this method, handsheets are printed with a full scale 4-colour sheet-fed offset printing machine using a commercial printing ink. The vessel picking printing test was performed for the unfractionated eucalyptus kraft pulps, the vessel-rich and vessel-poor fractions. The picked particles were analyzed and counted using an image analyzer. The vessel picking printing test was also done on the vessel-rich fractions after PFI-beating 2000 revolutions. Hydrocyclone separated the vessels according to their size and shape successfully. The microscopy analyze showed that vessels in the vessel-rich fraction were larger and more square-shaped than those in the vessel-poor pulp. The refining of the vessel-rich fraction decreased the vessel picking tendency to the same or even lower level than that of the unfractionated pulp.

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INTRODUÇÃO

A composição dos elementos da celulose influencia propriedades interativas do papel como resistência e ligação entre fibras (desempenho), aspereza superficial e resistência superficial (imprimibilidade). As propriedades dos elementos de vaso para a fabricação de papel são inferiores, pois que não se ligam bem e contribuem pouco para a resistência do papel. O arrancamento de vasos é fenômeno comum em papéis de imprimir que contêm celuloses de madeira de fibra curta. O problema do arrancamento de vasos é um fenômeno caracterizado pelo fato de que alguns dos elementos de vasos de madeiras de fibra curta na superfície do papel tendem a ser arrancados pela pegajosidade da tinta da impressora (Ohsawa, 1988). O arrancamento de vasos de folhosas na impressão offset de papéis de impressão não-revestidos caracteriza-se pelo surgimento de pequenas manchas brancas em áreas de uma só cor e de meio-tom da impressão. Esses defeitos irão se repetir exatamente na mesma área da impressão por várias centenas de impressões, mas por fim passarão a ser menores e menos intensos, até desaparecerem por completo. As formas dessas manchas brancas podem ser alongadas ou apresentar-se mais como quadrados, com dimensões da ordem de 1 mm ou menores. Vasos presentes na blanqueta de uma impressora offset convencional são intrinsecamente oleofóbicos devido ao umedecimento preferencial pela solução umedecedora. Esses vasos tornam-se oleofílicos e aceitam tinta somente após centenas de impressões. Normalmente, um problema de arrancamento de vasos se tornará evidente após a impressão de algumas centenas de folhas (Shallhorn, 1997).

É de conhecimento geral que a tendência ao arrancamento de vasos é causada principalmente pela presença de elementos de vaso de grandes dimensões em celuloses de madeiras de folhosas, tornando-se o problema mais crítico quando a coesão entre elementos de vaso e fibras for muito baixa (Ohsawa, 1988). Considera-se que a quantidade de elementos de vaso arrancados durante a impressão se deva aos seguintes fatores: 1) número, tamanho e formato dos elementos de vaso na superfície do papel; 2) resistência da coesão entre os elementos de vaso e a folha de papel e 3) número e resistência da ligação das fibras que estão cobrindo os elementos de vaso (Ohsawa, 1988; Colley, 1975).

Diminuição da tendência ao arrancamento de vasos de celuloses de madeiras de fibra curta pode ser conseguida mediante: 1) redução do teor de vasos na massa selecionando-se matéria-prima de madeira de fibra curta adequada, que tenha elementos de vaso pequenos e delgados e fibras conformativas (Ohsawa, 1988) ou a remoção de elementos de vaso de grandes dimensões e quadrados em sua forma por meio de hidrociclones (Ohsawa *et al.*, 1982; Mukoyoshi, Ohsawa, 1986; Mukoyoshi, 1986; Ohtake *et al.*, 1987; Ohtake, Okagawa, 1988); 2) a redução do tamanho dos elementos de vaso mediante refinação da celulose em alta consistência (Ohsawa *et al.*, 1984; Nanko *et al.*, 1988) ou refinação da celulose com

INTRODUCTION

The composition of pulp elements influences interacting paper properties like strength and bonding (runnability), surface roughness and surface strength (printability). Papermaking properties of vessel elements are inferior, since they do not bond well and contribute little to the strength of paper. The vessel picking is common problem in printing papers containing hardwood pulps. The vessel picking trouble is a phenomenon that some of the hardwood vessel elements in the paper surface tend to be picked off by an ink-tackiness of the printing press (Ohsawa, 1988). Hardwood vessel picking in the offset printing of uncoated fine papers is characterized by the appearance of small, white spots in solid and halftone areas in the print. These defects will repeat exactly in the same area of the print for several hundred impressions, but they will eventually become smaller and less intense until they fade away. The shapes of these white spots are either elongated or they may appear more as squares of the order of 1mm or less in dimension. Vessels on the blanket of a conventional offset press are intrinsically oleophobic because of preferential wetting by the fountain solution. These vessels become oleophilic and accept ink only after printing few hundred impressions. Thus, if a vessel picking problem is going to occur, it usually becomes evident after printing a few hundred sheets (Shallhorn, 1997).

It is generally known that vessel picking tendency is mainly caused by the presence of large vessel elements in hardwood pulps and the problem becomes more severe when the bonding strength between vessel elements and fibers is too weak (Ohsawa, 1988). The amount of vessel elements, which will be picked off during printing, is considered to be caused by the following factors, such as: 1) number, size and shape of the vessel elements in the paper surface; 2) bonding strength between vessel elements and paper sheet; and 3) number and bonding strength of fibers, which are covering vessel elements (Ohsawa, 1988; Colley, 1975).

*Reduction of vessel picking tendency of hardwood pulps can be achieved by: 1) reducing vessel content in a stock by selecting a suitable hardwood raw material, which has small and slender vessel elements and conformable fibers (Ohsawa, 1988) or removing large and square-shaped vessel elements by using hydrocyclones (Ohsawa *et al.*, 1982; Mukoyoshi, Ohsawa, 1986; Mukoyoshi, 1986; Ohtake *et al.*, 1987; Ohtake, Okagawa, 1988); 2) reducing size of the vessel elements by refining the pulp at high consistency (Ohsawa *et al.*, 1984; Nanko *et al.*, 1988) or refining the pulp with low refining intensity, i.e. low specific edge load (de Almeida et*

baixa intensidade de refinação, isto é, baixa carga específica nas lâminas (de Almeida *et al.*, 2006; Joy *et al.*, 2004); 3) aumento da coesão entre vasos e fibras por via do aumento da conformatividade das fibras utilizando-se polpa com alto teor de hemicelulose, mediante colagem superficial, através da refinação da celulose em alta consistência (Ohsawa *et al.*, 1986; Mukoyoshi *et al.*, 1986) ou tratando a celulose com carboximetilcelulose (Blomstedt *et al.*, 2008; Rakkolainen *et al.*, 2009); 4) formando uma estrutura adequada da folha, isto é, cobrindo os vasos com fibras (Nanko *et al.*, 1987); 5) arrancamento de vasos também pode ser reduzido por tratamento da celulose com enzimas (Uchimoto *et al.*, 1988). Além desses pré-tratamentos, tecnologias de fabricação de papel (caixa de entrada, máquina de papel, prensagem úmida, calandragem) e características da impressora (velocidade, temperatura, solução umedecedora, suprimento de tinta, tipo de tinta e limpeza de equipamentos) também influem no arrancamento de vasos.

Os vasos são compostos de células simples; seu tamanho e distribuição no anel de crescimento variam com a espécie. Elementos de vaso são mais curtos do que fibras de madeira de fibra curta e o diâmetro dos vasos varia grandemente de espécie para espécie (Ilvessalo-Pfäffli, 1995). Em geral, há de 3 a 25 vasos por mm² de seção transversal de xilema de eucalipto. Algumas espécies contêm mais vasos do que outras. Também há muita variação entre as dimensões de elementos de vaso, mas os vasos apresentam em sua maior parte um diâmetro compreendido na faixa de 60 a 250 µm e comprimento entre 200 e 600 µm. Madeiras ricas em vasos, que têm vasos muito largos em diâmetro, podem ter aproximadamente 25% a 30% de seu volume ocupado por esses elementos. Na maior parte das espécies comerciais de eucaliptos e seus clones, a proporção de vasos no volume da madeira varia de 10% a 20% (Foelkel, 2007).

A parede do vaso é relativamente fina, praticamente igual à espessura da parede da fibra, entre 2,5 e 5 µm. A composição química dos vasos é semelhante em seus constituintes químicos, mas há alguma diferença entre fibras e vasos. Verificou-se que elementos de vaso são mais ricos em celulose em comparação com fibras, e lignina tem sido encontrada nos elementos de vaso até mesmo após o branqueamento (Fardim, Lidström, 2009). Também há indicações de que a lignina presente nos vasos é mais hidrofóbica, mais rica em unidades de guaiacil do que de siringil (Watanabe, 2004). A relação entre siringil e guaiacil pode atingir cerca de 0,5 a 1 para os vasos, enquanto a das fibras varia de 2 a 6 (Foelkel, 2007). Tem sido também constatado que o conteúdo de xilana dos elementos de vaso é mais elevado do que aquele das fibras (Figueiredo Alves *et al.*, 2009).

Aparelho de laboratório para teste de imprimibilidade não é confiável para análise de tendência ao arrancamento de vasos em papéis de impressão comerciais, nem mesmo em celulosas diferentes, pois a área de papel impressa é demasiado pequena - tira de 2,5 cm de largura e 30 cm de comprimento -, para de-

al., 2006; Joy *et al.*, 2004); 3) increasing vessel to fiber bonding strength by increasing the conformability of fibers, by using pulp with high hemicellulose content, by surface sizing, by refining the pulp at high consistency (Ohsawa *et al.*, 1986; Mukoyoshi *et al.*, 1986) or by treating the pulp with carboxymethyl cellulose (Blomstedt *et al.*, 2008; Rakkolainen *et al.*, 2009); 4) forming a suitable sheet structure, i.e. covering the vessel elements with fibers (Nanko *et al.*, 1987); 5) vessel picking can also be reduced by treating the pulp with enzymes (Uchimoto *et al.*, 1988). Besides these pretreatments paper manufacturing technologies (headbox, paper machine, wet pressing, calendering) and printing machine characteristics (speed, temperature, fountain solution, ink supply, ink type and equipment cleanliness) affect the vessel picking.

The vessels are composed of single cells; their size and distribution within the growth ring vary with species. Vessel elements are shorter than hardwood fibers, and the diameter of vessels varies greatly from species to species (Ilvessalo-Pfäffli, 1995). In general, there is about 3 to 25 vessels per mm² of eucalyptus xylem cross section. Some species have more vessels than others. There is also much variation between the dimensions of vessel elements, but vessels have mostly a diameter ranging from 60 to 250 µm and a length between 200 to 600 µm. Vessel rich woods having very wide vessels in their diameter may have approximately 25% to 30% of their volume occupied by the vessels. In most commercial eucalyptus species and clones the proportion of vessels in the wood volume ranges from 10% to 20% (Foelkel, 2007).

The vessel wall is relatively thin, practically equal to the fiber wall thickness, between 2.5 and 5 µm. The chemical composition of the vessels is similar in its chemical constituents, but there is some difference between fibers and vessels. Vessel elements have been found to be richer in cellulose compared with fibers, and lignin has been found in the vessel elements even after bleaching (Fardim, Lidström, 2009). There are also indications that the lignin in vessels is more hydrophobic, richer in guaiacyl units than in syringyl (Watanabe, 2004). The syringyl to guaiacyl ratio may reach about 0.5 to 1 for the vessels, while that of the fibers is from 2 to 6 (Foelkel, 2007). It has been also revealed that the xylan content of vessel elements is higher than that of the fibers (Figueiredo Alves *et al.*, 2009).

A laboratory printability tester is not reliable to analyze the vessel picking tendency of commercially made fine papers, or not even different pulps, because the area of paper printed is too small - 2,5 cm wide and 30 cm long strip -, to capture the statistically rare

teectar o defeito estatisticamente raro de arrancamento de vasos. Neste estudo, a tendência ao arrancamento de vasos foi analisada mediante a impressão de folhas manuais em laboratório com impressora offset plana, de 4 cores, em escala natural e com utilização de tinta de impressão comercial. Os objetivos deste estudo foram de avaliar os efeitos do conteúdo de vasos, do tamanho dos vasos, do formato dos vasos e da refinação da celulose sobre a tendência ao arrancamento de vasos. Foi igualmente determinada a composição química de frações livres de vasos e ricas em vasos. A avaliação da tendência ao arrancamento de vasos foi realizada através de método desenvolvido no KCL.

MATERIAIS E MÉTODOS

Matéria-prima

As polpas industriais kraft branqueadas de eucalipto utilizadas nos ensaios foram de *Eucalyptus globulus*, procedente da Europa meridional, e de *Eucalyptus grandis*, proveniente da América do Sul. Ambas as celuloses foram secadas na fábrica.

Fracionamento

As celuloses secas de fábrica foram deixadas para inchar durante a noite e na manhã seguinte foram desagregadas utilizando um desagregador de 50 litros. O tempo de desagregação foi de 15 minutos e a consistência de 5%.

As polpas foram fracionadas por meio de hidrociclone Bauer de 3". Os ensaios foram realizados com consistência da celulose de alimentação de 0,1% e pressão diferencial de 1,6 bar. A configuração do ensaio para *Eucalyptus globulus* está representada na **Figura 1**. Neste artigo, a celulose de eucalipto suprida ao hidrociclone é chamada de celulose de alimentação, a celulose do aceito é chamada de fração pobre em vasos e a celulose do rejeito é chamada de fração rica em vasos.

Celulose de *Eucalyptus globulus* foi fracionada em sistema de dois estágios (Figura 1). O rejeito do primeiro estágio foi o material alimentado ao segundo estágio. A celulose do aceito

vessel pick defect. In this study, the vessel picking tendency was analyzed by printing laboratory handsheets with a full scale printing machine, 4-colour sheet-fed offset printing press, and using a commercial printing ink. The objectives of this study were to evaluate the effects of vessel content, vessel size, vessel shape, and pulp refining on the vessel picking tendency. Also the chemical composition of the vessel-free and vessel-rich fraction was determined. The evaluation of the vessel picking tendency was performed using a method developed at KCL.

MATERIALS AND METHODS

Raw material

The bleached eucalyptus kraft mill pulps used in the trials were *Eucalyptus globulus* from South Europe and *Eucalyptus grandis* from South America. Both pulps were mill-dried.

Fractionation

The mill-dried pulps were allowed to swell over night, and the next morning they were disintegrated using 50-litre disintegrator. The disintegration time was 15 minutes and consistency 5%.

The pulps were fractionated using Bauer 3" hydrocyclone. Trials were performed with the feed pulp consistency of 0.1%, and the pressure difference was 1.6 bar. The trial configuration for *Eucalyptus globulus* is shown in **Figure 1**. The eucalyptus pulp that was fed to the hydrocyclone is called feed pulp, the accept pulp is called vessel-poor fraction, and the reject pulp is called vessel-rich pulp in this paper.

Eucalyptus globulus was fractionated in a two-stage system (Figure 1). The reject of the first stage was the feed of the second stage. The accept pulp

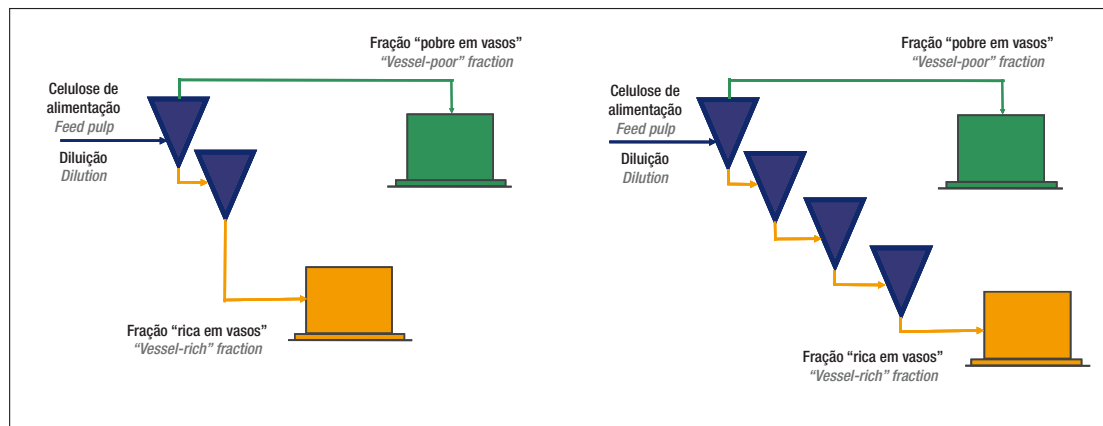


Figura 1. Configurações de testes para *Eucalyptus globulus* (à esquerda) e para *Eucalyptus grandis* (à direita)
Figure 1. Trial configurations for *Eucalyptus globulus* (on the left), and for *Eucalyptus grandis* (on the right)

do segundo estágio não foi recuperada. Celulose de *Eucalyptus grandis* foi fracionada em sistema de quatro estágios (Figura 1). O rejeito do primeiro estágio foi o material alimentado ao segundo estágio, o rejeito do segundo estágio foi o material alimentado ao terceiro estágio, e assim sucessivamente. Também neste caso, as celuloses do aceito do segundo, do terceiro e do quarto estágios não foram recuperadas.

Após cada estágio de fracionamento as amostras de celulose foram analisadas com analisador Kajaani FS-300, sendo determinados o número de elementos de vaso e seu comprimento e largura. Isso foi feito para monitorar a eficiência de separação.

Análises

O cálculo dos tipos de células da composição (fibras, vasos e células de raios), SCAN-G3:90, foi realizado para as celuloses de alimentação e das frações ricas em vasos e pobres em vasos. Comprimento e largura dos vasos também foram determinados utilizando-se um fotomicroscópio, tendo sido medidos 300 vasos.

As celuloses de alimentação e das frações ricas e pobres em vasos foram submetidas às seguintes análises químicas:

- Lignina residual total, ligninas Klason e solúvel em ácido (método interno KCL, TAPPI T222 modificado)
- Ácidos urônicos (método interno KCL, SCAN Forsk 737)
- Extratos de acetona (SCAN-CM 49)
- Composição de carboidratos (TAPPI T249, modificado)

Antes dessas análises, os finos foram removidos das amostras de celulose.

Teste de arrancamento de vasos

As celuloses de alimentação e as celuloses pobres e ricas em vasos foram usadas na condição de não-refinadas. Além disso, as frações ricas em vasos foram refinadas em moinho PFI nível 2000 revoluções, a fim de verificar o efeito da refinação sobre os vasos.

Folhas manuais foram formadas de acordo com norma EN ISO 5269-1 com celuloses de alimentação, das frações pobres em vasos e ricas em vasos, todas não-refinadas, e também das frações ricas em vasos refinadas; cinco folhas para cada amostra. A gramatura-alvo das folhas foi de 60 g/m².

As folhas manuais foram calandradas em calandra para folhas. As condições de calandragem foram: pressão linear de 94 kN/m (15 bar), 1 nip. As folhas de laboratório calandradas foram fixadas com fita a uma folha-suporte. As folhas foram impressas em impressora offset plana, de 4 cores, com utilização de tinta de impressão comercial e um nip de suporte traseiro. Marcas de arrancamento foram coletadas da blanqueta com de fitas adesivas. As fitas foram analisadas por meio de analisador de imagens para contagem da tendência ao arrancamento, sendo: quantidade total de arrancamentos/cm² e área arrancada em µm. Como o método é trabalhoso, não foram feitas medições paralelas, de modo que a confiabilidade do método não pode ser estimada adequadamente.

from the second stage was not recovered. Eucalyptus grandis was fractionated in a four-stage system (Figure 1). The reject of the first stage was the feed of the second stage, and the reject of the second stage was the feed of the third stage, etc. Also in this case the accept pulp from the second, third and fourth stages were not recovered.

After each fractionation stage the pulp samples were analyzed with Kajaani FS-300, and the number of vessel elements, length and width was determined. This was done to monitor the separation efficiency.

Analyses

Calculation of cell type composition (fibers, vessels and ray cells), SCAN-G3:90, was performed for the feed pulps, vessel-rich and vessel-poor fractions. The vessel length and width was also determined using light microscope, 300 vessels were measured.

The following chemical analyses were conducted on the feed, vessel-rich and vessel-poor fractions:

- Total residual lignin, Klason and acid soluble lignin (KCL internal method, TAPPI T222 modified)
- Uronic acids (KCL internal method, SCAN Forsk 737)
- Acetone extracts (SCAN-CM 49)
- Carbohydrate composition (TAPPI T249, modified)

Before these analyses the fines were removed from the pulp samples.

Vessel picking test

The feed pulps, vessel-poor and vessel-rich pulps were used as unrefined. In addition, the vessel-rich fractions were refined using PFI-mill for 2000 revolutions in order to see the effect of the refining on the vessels.

Handsheets were formed according to standard EN ISO 5269-1 from the unrefined feed pulps, vessel-poor and vessel-rich fractions and also from the refined vessel-rich fractions, five sheets for each sample. Target grammage of the sheets was 60 g/m².

The handsheets were calendered with a sheet calender. The calendering conditions were as follows: line pressure of 94 kN/m (15 bar), 1 nip. The calendered laboratory sheets were taped to a carrier sheet. The sheets were printed with a 4-colour sheet-fed offset printing press using a commercial printing ink and one back-trap nip. Pick marks were collected from the blanket with adhesive tapes. The tapes were analyzed with an image analyzer to count picking tendency: total number of picks/cm² and picked area µm. As the method is laborious no parallel measurement were done, so the reliability of the method cannot be properly estimated.

RESULTADOS E DISCUSSÃO

Composição de tipos de células

Enriquecimento dos elementos de vasos foi bem-sucedido na fração de rejeito. Ohsawa *et al.* (Ohsawa, 1982) também constataram ser possível separar elementos de vasos pela ação de um hidrociclone e que os elementos de vasos são acumulados à fração de rejeito. A **Tabela 1** e a **Tabela 2** mostram a composição de tipos de células de celuloses de *Eucalyptus globulus* e *Eucalyptus grandis*, respectivamente.

Quando o processamento em hidrociclone foi realizado em sistema de dois estágios, Tabela 1, foi possível aumentar o teor de vasos da celulose de 0,4% (m/m) para 1,2% (m/m). No sistema de quatro estágios o teor de vasos da celulose aumentou de 0,5% (m/m) para 4,0% (m/m), Tabela 2. Eficiência de separação algo melhor é encontrada na literatura, Ohsawa *et al.* (Ohsawa, 1984). Em seu estudo, os elementos de vasos foram separados com um hidrociclone Centricleaner 600 – que é um hidrociclone mais eficiente do que aquele usado neste estudo – a partir de celulose de eucalipto, tendo conseguido enriquecer a fração de rejeito para aproximadamente 5,7% em peso de vasos.

A Tabela 1 e a Tabela 2 indicam que os conteúdos de células de raio das frações pobres em vasos eram mais altos do que os das frações ricas em vasos. No caso de *Eucalyptus grandis* o teor de células de raio da fração pobre em vasos era até mesmo superior ao da celulose de alimentação. O enriquecimento de células de raio para a fração de aceito foi também visto anteriormente (Panula-Ontto 2002).

O cálculo dos elementos de vasos apresentou valores mais altos após a refinação (**Tabela 3**). Isso devido ao fato de a

RESULTS AND DISCUSSION

Cell type composition

Enrichment of the vessel elements succeeded to the reject fraction. Ohsawa *et al.* (Ohsawa, 1982) had also found that it is possible to separate vessel elements by hydrocycloning, and that the vessel elements are accumulated to the reject fraction. **Table 1** and **Table 2** show the cell type composition of *Eucalyptus globulus* and *Eucalyptus grandis*, respectively.

When the hydrocycloning was performed in a two-stage system, Table 1, it was possible to increase the vessel content of the pulp from 0.4% (m/m) to 1.2% (m/m). In the four-stage system the vessel content of the pulp increased from 0.5% (m/m) to 4.0% (m/m), Table 2. Somewhat better separation efficiency is found from the literature, Ohsawa *et al.* (Ohsawa, 1984). In their study, vessel elements were separated with a hydrocyclone Centricleaner 600 - which is more efficient hydrocyclone than the one used in this study -, from eucalyptus pulp and succeeded to enrich about 5.7 weight % of vessels to the reject fraction.

Table 1 and Table 2 show that the ray cells content of the vessel-poor fractions were higher than that of the vessel-rich fractions. In the case of *Eucalyptus grandis* the ray cell content of the vessel-poor fraction was even higher than that of the feed pulp. The enrichment of ray cells to the accept fraction has also been seen earlier (Panula-Ontto 2002).

The calculation of the vessel elements showed higher values after the refining (**Table 3**). This is because in the

Tabela 1. Composição de tipos de células de *Eucalyptus globulus* / **Table 1.** Cell type composition of *Eucalyptus globulus*

m/m, %	Alimentação / Feed	Pobre em vasos / Vessel-poor	Rica em vasos / Vessel-rich
Fibras / Fibers	96,5	97,4	98,4
Vasos / Vessels	0,4	0,2	1,2
Células de raio / Ray cells	3,1	2,4	0,4

Tabela 2. Composição de tipos de células de *Eucalyptus grandis* / **Table 2.** Cell type composition of *Eucalyptus grandis*

m/m, %	Alimentação / Feed	Pobre em vasos / Vessel-poor	Rica em vasos / Vessel-rich
Fibras / Fibers	96,7	95,5	96
Vasos / Vessels	0,5	0,4	4,0
Células de raio / Ray cells	2,8	4,1	traços

Tabela 3. Teor de vasos das celuloses não-refinada e refinada de *Eucalyptus grandis*

Table 3. Vessel content of the unrefined and refined pulps, *Eucalyptus grandis*

m/m, %	Não-refinada rica em vasos / Unrefined vessel-rich	Refinada rica em vasos / Refined vessel-rich
Fibras / Fibers	96	95,1
Vasos / Vessels	4,0	4,9
Células de raio / Ray cells	traços	-



Figura 3. Fração rica em vasos de *Eucalyptus globulus* refinada / **Figure 3.** Refined *Eucalyptus globulus* vessel-rich fraction

refinação romper e dividir os vasos, da forma representada na **Figura 3**.

Ohsawa *et al.* (Ohsawa, 1984) também constataram que refinação a consistência particularmente alta reduz o arrancamento de vasos. Em seu estudo, as celuloses foram refinadas em moinho PFI, com consistência de 10% ou 20%. Segundo eles, celulose refinada a alta consistência continha mais fibras fibriladas e vasos fibrilados. Neste estudo não foi detectada fibrilação de elementos de vasos (Figura 3).

Dimensões dos vasos

A **Tabela 4** e a **Tabela 5** indicam que o hidrociclone separou os vasos segundo seu tamanho. As frações ricas em vasos os tinham mais largos do que as outras celuloses. O comprimento dos vasos era aproximadamente o mesmo em todas as celuloses. Além disso, os vasos das frações ricas

refining the vessels were broken and split as shown in Figure 3.

Ohsawa et al. (Ohsawa, 1984) has also seen that especially high consistency refining decrease vessel picking. In their study the pulps were beaten at PFI mill using consistency of 10% or 20%. According to them, high consistency refined pulp contained more fibrillated fibers and fibrillated vessels. In this study fibrillation of vessel elements was not detected (Figure 3).

Dimension of vessels

Table 4 and Table 5 show that hydrocyclone separated the vessels according to their size. The vessel-rich fractions had wider vessels than the other pulps. The length of the vessels was about the same in all the pulps. In addition, the vessels of the vessel-rich fractions were

Tabela 4. Dimensões dos vasos de *Eucalyptus globulus* / **Table 4.** Vessel dimension of *Eucalyptus globulus*

Dimensões dos vasos, μm Vessel dimension, μm	Alimentação Feed	Pobre em vasos Vessel-poor	Rica em vasos não-refinada Unrefined vessel-rich	Rica em vasos refinada Refined vessel-rich
Comprimento / Length	305	293	307	334
Largura / Width	178	153	190	171
Largura/comprimento / Width/length	0,58	0,52	0,62	0,51

Tabela 5. Dimensões dos vasos de *Eucalyptus grandis* / **Table 5.** Vessel dimension of *Eucalyptus grandis*

Dimensões dos vasos, μm Vessel dimension, μm	Alimentação Feed	Pobre em vasos Vessel-poor	Rica em vasos não-refinada Unrefined vessel-rich	Rica em vasos refinada Refined vessel-rich
Comprimento / Length	357	346	368	394
Largura / Width	179	167	208	220
Largura/comprimento / Width/length	0,50	0,48	0,57	0,56

em vasos apresentavam um formato mais quadrado (largura/comprimento) do que os da celulose de alimentação e da celulose pobre em vasos. A mesma observação tem sido feita também por Mukoyoshi *et al.* (Mukoyoshi, 1986).

A Tabela 4 e a Tabela 5 também mostram que as dimensões e a forma dos elementos de vasos eram diferentes após a refinação, pois os vasos foram rompidos e divididos na refinação. A relação entre largura e comprimento era menor, o que significa que os vasos não apresentavam uma forma tão quadrada quanto antes da refinação.

Composição química das celuloses

A composição dos polissacarídeos e o conteúdo de lignina das diversas celuloses não apresentou quaisquer diferenças, apesar do enriquecimento de vasos. O teor de extrativos estava abaixo do limite de determinação em todos os casos. A única diferença foi vista no teor de ácido hexenurônico. A fração rica em vasos de celulose de *Eucalyptus grandis* continha mais ácido hexenurônico (11 mmol/kg) do que a celulose de alimentação de *Eucalyptus grandis* (7,2 mmol/kg) e a fração pobre em vasos dessa celulose, abaixo do limite de determinação, de 4,5 mmol/kg. Um teor mais alto de xilana da celulose rica em vasos foi revelada anteriormente (Figueiredo Alves *et al.*, 2009), e é conhecido que ácido metilglucurônico, o grupo lateral em xilana nativa, é parcialmente convertido em ácido hexenurônico durante o cozimento kraft (Teleman *et al.*, 1995, Danielson, 2007). Com base nessas informações, é provável que a fração rica em vasos pudesse ter um teor de ácido hexenurônico mais alto do que a fração pobre em vasos. Contudo, é de se ter em mente que essa diferença não se deve necessariamente aos elementos de vasos, porque o teor de vasos da fração rica em vasos, de 4% (m/m), ainda era razoavelmente baixo.

Tendência ao arrancamento de vasos das celuloses

A **Figura 4** apresenta as fotos das folhas impressas, *Eucalyptus grandis*.

Áreas arrancadas são representadas como pontos brancos nas folhas manuais. As fotos das folhas manuais de celulose de alimentação (Figura 4, à esquerda) e da fração pobre em vasos

more square-shaped (width/length) than those of the feed pulp and those of the vessel-poor pulp. The same observation has been made also by Mukoyoshi et al. (Mukoyoshi, 1986).

Table 4 and Table 5 also show that the dimensions and the shape of the vessel elements were different after the refining, because the vessel were broken and split in the refining. Width/length ratio was lower, which means that the vessels were not so much square-shaped than before the refining.

Chemical composition of the pulps

The polysaccharide composition and the lignin content of the various pulps did not show any differences despite the enrichment of the vessels. The content of extractives was below determination limit in all the cases. The only difference was seen in the content of hexenuronic acid. The Eucalyptus grandis vessel-rich pulp contained more hexenuronic acid (11 mmol/kg) than the Eucalyptus grandis feed pulp (7.2 mmol/kg), and the vessel-poor pulp below determination limit, 4.5 mmol/kg. Higher xylan content of vessel rich pulp has earlier been revealed (Figueiredo Alves et al., 2009), and it is known that methylglucuronic acid, the side group in native xylan, is partly converted into hexenuronic acid during kraft cooking (Teleman et al., 1995, Danielson, 2007). Based on this information it is likely that the vessel-rich fraction could have higher hexenuronic acid content than the vessel-poor fraction. However, it should be kept in mind that this difference is not necessarily due to the vessel elements, because the vessel content of the vessel rich fraction was still fairly low, 4 % (m/m).

Vessel picking tendency of the pulps

Figure 4 shows the pictures taken from the printed sheets, Eucalyptus grandis.

Picked areas are shown as white spots in the handsheets. The picture taken from the handsheet made from the feed pulp (Figure 4 on the left) and the vessel-poor

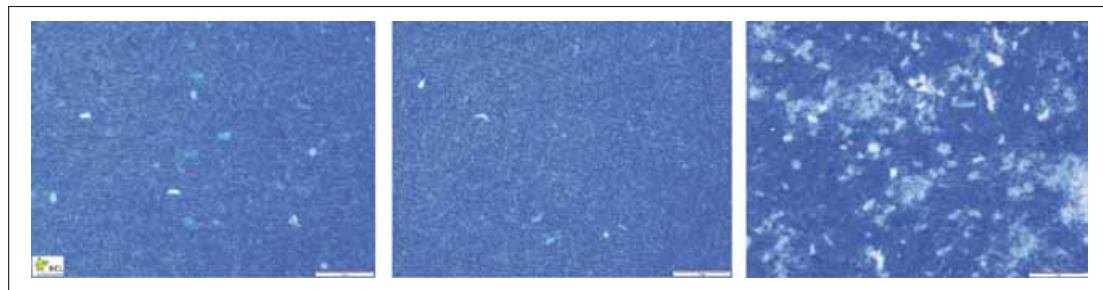


Figura 4. Folha manual impressa de celulose de alimentação (à esquerda), da fração pobre em vasos (no centro) e da fração rica em vasos (à direita), de *Eucalyptus grandis* / **Figure 4.** Printed handsheet of the feed pulp (on the left), of the vessel-poor fraction (in the middle), of the vessel-rich fraction (on the right), *Eucalyptus grandis*

(Figura 4, no centro) são quase idênticas. Em comparação com a folha manual de celulose pobre em vasos, a folha manual de celulose de alimentação continha quantidade um pouco maior de marcas de arrancamento, que também eram um pouco maiores.

A folha feita com a fração rica em vasos (Figura 4, à direita) tinha um número de elementos de vaso tão alto nas folhas impressas que as marcas de arrancamento chegaram a se constituir em áreas grandes, e não em manchas. Quando as marcas de arrancamento eram observadas com lupa era notado que os vasos arrancados tinham arrastado fibras da superfície do papel.

As marcas de arrancamento coletadas da blanda de impressão foram contadas com um analisador de imagens. A quantidade total de arrancamentos/cm² nas celulosas de *Eucalyptus grandis* de alimentação e da fração pobre em vasos foi de 5,3 e 3,6, respectivamente (Tabela 6). A fração de celulose *Eucalyptus grandis* rica em vasos continha número excessivo de arrancamentos para que pudesse ser avaliada com o analisador de imagens. A área arrancada da fração de celulose de *Eucalyptus grandis* pobre em vasos era claramente menor do que aquela da celulose de alimentação, 0,11 µm² contra 0,26 µm².

O número total de arrancamentos/cm² nas celulosas de *Eucalyptus globulus* de alimentação, da fração pobre em vasos e da fração rica em vasos foi de 6,4; 4,7 e 27,0, respectivamente (Tabela 7).

fraction (Figure 4 in the middle) are almost alike. The handsheet made from the feed pulp contained somewhat more, and showed a little greater pick marks than the sheet made from the vessel-poor pulp.

The sheet made from the vessel-rich fraction (Figure 4 on the right) had so high a number of vessel elements in the printed sheets that the pick marks are shown as big areas rather than spots. When the pick marks were observed with a loupe, it was noticed that the picked vessels had also released fibers with them from the paper surface.

The collected pick marks from the printing blanket were counted with an image analyzer. The total number of picks/cm² in the feed and vessel-poor Eucalyptus grandis pulp was 5.3 and 3.6, respectively (Table 6). The vessel-rich Eucalyptus grandis pulp contained too many picks to be analyzed with the image analyzer. The picked area of the vessel-poor Eucalyptus grandis pulp was clearly lower than that of the feed pulp, 0.11 µm² vs. 0.26 µm².

The total number of picks/cm² in the feed, vessel-poor and vessel-rich Eucalyptus globulus pulp was 6.4; 4.7 and 27.0, respectively (Table 7).

Tabela 6. Resultados de arrancamento de vasos para *Eucalyptus grandis* / **Table 6.** Vessel picking results for *Eucalyptus grandis*

Número de arrancamentos/cm ² Number of picks/cm ²	Alimentação Feed	Pobre em vasos Vessel-poor	Rica em vasos Vessel-rich
Tinta Ink	3,2	2,3	Excesso de arrancamentos para contar Too many picks to count
Suporte traseiro Back trap	2,1	1,3	Excesso de arrancamentos para contar Too many picks to count
Total Total	5,3	3,6	Excesso de arrancamentos para contar Too many picks to count
Área arrancada, µm ² / Picked area, µm ²			
Tinta Ink	0,20	0,08	Excesso de arrancamentos para contar Too many picks to count
Suporte traseiro Back trap	0,06	0,03	Excesso de arrancamentos para contar Too many picks to count
Total Total	0,26	0,11	Excesso de arrancamentos para contar Too many picks to count

Tabela 7. Resultados de arrancamento de vasos para *Eucalyptus globulus* / **Table 7.** Vessel picking results for *Eucalyptus globulus*

Número de arrancamentos/cm ² Number of picks/cm ²	Alimentação Feed	Pobre em vasos Vessel-poor	Rica em vasos Vessel-rich
Tinta / Ink	4,1	3,0	16,2
Suporte traseiro / Back trap	2,2	1,7	10,8
Total / Total	6,4	4,7	27,0
Área arrancada, µm ² / Picked area, µm ²			
Tinta / Ink	0,19	0,12	1,09
Suporte traseiro / Back trap	0,04	0,03	0,35
Total / Total	0,23	0,15	1,44

A área arrancada da celulose de *Eucalyptus globulus* rica em vasos era 14 vezes maior do que a da celulose de alimentação. A área arrancada da celulose de *Eucalyptus globulus* pobre em vasos era inferior à da polpa de alimentação, $0,15 \mu\text{m}^2$ contra $0,23 \mu\text{m}^2$.

Efeito da refinação no arrancamento de vasos

A literatura faz saber que refinação a consistência particularmente alta é efetiva na destruição de elementos de vaso, e que pode reduzir consideravelmente o teor de elementos grandes de vaso. Independentemente dos métodos de refino, a destruição de elementos de vaso atinge certo nível com CSF 400 mL (Canadian Standard Freeness), e refinação ulterior causa apenas pequena alteração no tamanho dos elementos de vaso (Nanko, 1988). Neste estudo, as celuloses ricas em vasos foram refinadas em moinho PFI (consistência de refinação de 10%), nível 2000 revoluções, e após essa refinação foi determinada a tendência ao arrancamento.

As **Figuras 7 e 8** reproduzem as fotos de folhas manuais impressas produzidas com fração rica em vasos não-refinada e refinada das celuloses de *Eucalyptus globulus* e *Eucalyptus grandis*, respectivamente.

Mediante a refinação da fração de *Eucalyptus globulus* rica em vasos, o número de arrancamentos/cm² foi reduzido

The picked area of the vessel-rich Eucalyptus globulus pulp was 14 times greater than that of the feed pulp. The picked area of the vessel-poor Eucalyptus globulus pulp was lower than that of the feed pulp, $0.15 \mu\text{m}^2$ vs. $0.23 \mu\text{m}^2$.

Effect of the refining on the vessel picking

It is known from the literature that especially high consistency refining is effective for vessel element destruction and that it can reduce the content of large vessel elements considerably. Regardless of refining methods, the destruction of vessel elements reaches a certain level at CSF 400 mL, and further refining gives only small change in the size of the vessel element (Nanko, 1988). In this study the vessel-rich pulps were refined in a PFI-mill (refining consistency 10%) for 2000 revolutions and after the refining the picking tendency was determined.

Figures 7 and 8 show the picture taken from the printed handsheets made from the unrefined and the refined vessel-rich fraction, Eucalyptus globulus and Eucalyptus grandis, respectively.

By refining the Eucalyptus globulus vessel-rich frac-

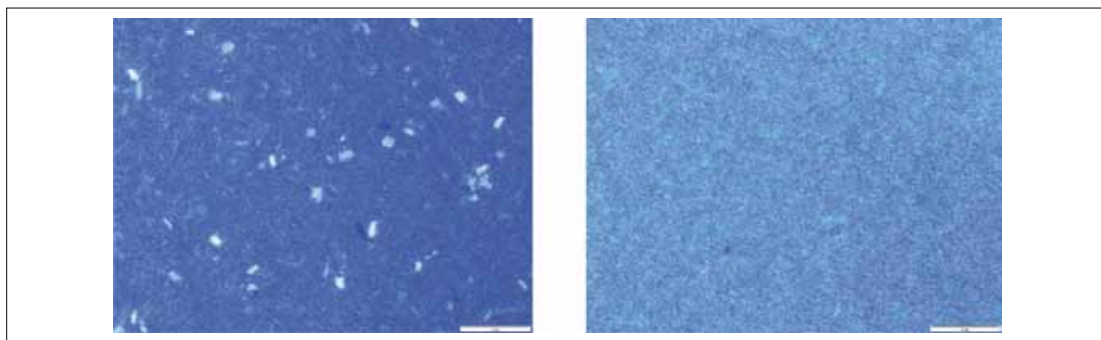


Figura 7. Folha manual impressa produzida com fração rica em vasos não-refinada (à esquerda) e refinada (à direita), de *Eucalyptus globulus*
Figure 7. Printed handsheet made from unrefined (on the left) and refined (on the right) *Eucalyptus globulus* vessel-rich fraction

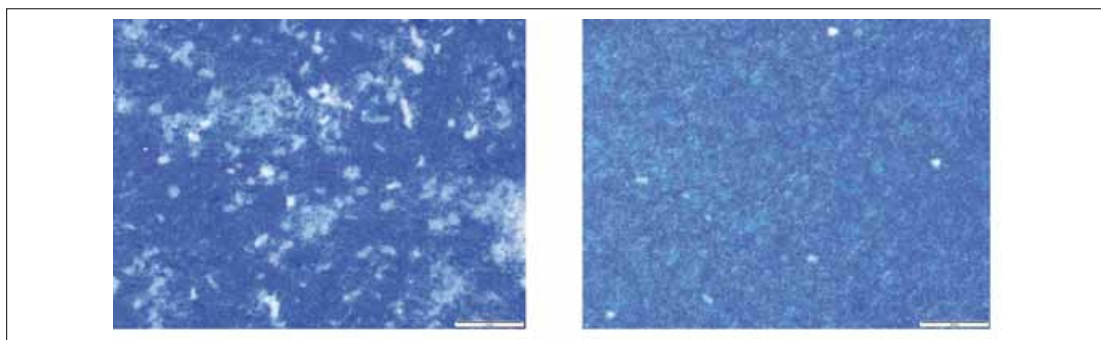


Figura 8. Folha manual impressa produzida com fração rica em vasos não refinada (à esquerda) e refinada (à direita), de *Eucalyptus grandis*
Figure 8. Printed handsheet made from unrefined (on the left) and refined (on the right) *Eucalyptus grandis* vessel-rich fraction

Tabela 8. Resultados de arrancamento de vasos para celuloses de *Eucalyptus globulus* de alimentação, pobre em vasos, rica em vasos não-refinada e refinada / **Table 8.** Vessel picking results for *Eucalyptus globulus* feed pulp, vessel-poor, unrefined and refined vessel-rich fraction

Número de arrancamentos/cm ² Number of picks/cm ²	Alimentação Feed	Pobre em vasos Vessel-poor	Rica em vasos não-refinada Unrefined vessel-rich	Rica em vasos refinada Refined vessel-rich
Tinta	4,1	3,0	16,2	1,2
Suporte traseiro	2,2	1,7	10,8	1,1
Total	6,4	4,7	27,0	2,3
Área arrancada, µm ² / Picked area, µm ²				
Tinta	0,19	0,12	1,09	0,03
Suporte traseiro	0,04	0,03	0,35	0,02
Total	0,23	0,15	1,44	0,05

Tabela 9. Resultados de arrancamento de vasos para celulose de *Eucalyptus grandis* de alimentação e da fração rica em vasos refinada / **Table 9.** Vessel picking results for *Eucalyptus grandis* feed pulp and refined vessel-rich fraction

Número de arrancamentos/cm ² Number of picks/cm ²	Alimentação Feed	Rica em vasos refinada Refined vessel-rich
Tinta	3,2	4,2
Suporte traseiro	2,1	2,8
Total	5,3	7,0
Área arrancada, µm ²		
Tinta	0,20	0,22
Suporte traseiro	0,06	0,10
Total	0,26	0,32

de 27,0 para 2,3 (Tabela 8). Como mostrado anteriormente, os vasos foram rompidos (Figura 3) na refinação e já não se apresentavam num formato tão quadrado quanto antes do refino. Esta foi uma razão para redução na tendência ao arrancamento. Além disso, a conformatividade das fibras aumenta na refinação, assim como aumenta a resistência da ligação entre vasos e fibras (Ohsawa *et al.*, 1984, Ohsawa, 1988, Colley 1975).

Após a refinação, o número de arrancamentos/cm² era inferior ao da celulose de alimentação não-refinada e até mesmo inferior ao da celulose pobre em vasos. O número de arrancamentos/cm² da celulose de alimentação, da fração pobre em vasos e da fração rica em vasos refinada era de 6,4; 4,7 e 2,3, respectivamente. Da mesma forma, a área arrancada diminuiu significativamente na refinação, de 1,44 µm² para 0,05 µm², sendo inferior à da celulose de alimentação (0,23 µm²) e à da celulose pobre em vasos (0,15 µm²).

O número de arrancamentos/cm² e a área arrancada diminuíram na refinação da fração rica em vasos de celulose de *Eucalyptus grandis*. Todavia, a quantidade total de arrancamentos/cm² da fração rica em vasos refinada de celulose de *Eucalyptus grandis* era de 7,0 (Tabela 9). Isso ainda é cerca de 30% superior à da celulose de alimentação. Da mesma forma, a área total arrancada era cerca de 20% superior na fração rica em vasos refinada do que na celulose de alimentação.

tion, the number of picks/cm² was reduced from 27.0 picks/cm² to 2.3 picks/cm² (Table 8). As shown earlier, the vessels were broken (Figure 3) in the refining and they were not so much square-shaped than before the refining. This was one reason to reduced picking tendency. In addition, the conformability of the fibers is increased in the refining, and also vessel-to-fiber bonding strength is increased (Ohsawa et al., 1984, Ohsawa, 1988, Colley 1975).

After refining, the number of picks/cm² was lower than that in the unrefined feed pulp and also even lower than that in the vessel-poor pulp. The number of picks/cm² of the feed pulp, vessel-poor pulp and refined vessel-rich fraction was 6.4, 4.7 and 2.3, respectively. Also, the picked area decreased remarkably in the refining, from 1.44 µm² to 0.05 µm², and it was lower than that of the feed pulp (0.23 µm²) and that of the vessel-poor pulp (0.15 µm²).

*The number of picks/cm² and the picked area decreased in the refining of *Eucalyptus grandis* vessel-rich fraction. However, the total number of picks/cm² of the refined *Eucalyptus grandis* vessel-rich fraction was 7.0 (Table 9). This is still about 30% higher than that of the feed pulp. Also, the total picked area was about 20% higher for the refined vessel-rich fraction than that of the feed pulp.*

CONCLUSÕES

Celuloses industriais kraft branqueadas de eucalipto - *Eucalyptus globulus* e *Eucalyptus grandis* -, foram fracionadas utilizando um hidrociclone. A tendência ao arrancamento de vasos foi analisada através da impressão de folhas manuais com impressora offset plana de 4 cores, em escala natural, e utilizando tinta de impressão comercial. O hidrociclone separou os vasos segundo seu tamanho e formato; a fração rica em vasos possuía vasos maiores e de formato mais quadrado do que a fração pobre em vasos. As celuloses ricas em vasos apresentaram um número maior de arrancamentos/cm² e também área arrancada maior do que as celuloses de alimentação e as celuloses pobres em vasos. Na refinação, os vasos foram rompidos e divididos e a resistência da ligação das fibras foi aumentada. Em consequência, a refinação da fração rica em vasos reduziu a tendência ao arrancamento de vasos para o mesmo nível, se não mesmo inferior, ao da polpa não-fracionada. Também a área das marcas de arrancamento diminuiu. Este estudo tem provado que o método desenvolvido no KCL avalia corretamente a tendência ao arrancamento de vasos das diversas celuloses. Também demonstrou que a técnica de fracionamento possibilita o estudo de celuloses com vários conteúdos de vasos, a composição química dessas celuloses e o efeito de um tratamento separado dessas celuloses sobre a tendência ao arrancamento de vasos. ▲

CONCLUSIONS

Bleached Eucalyptus kraft mill pulps - *Eucalyptus globulus* and *Eucalyptus grandis* -, were fractionated using hydrocyclone. The vessel picking tendency was analyzed by printing the handsheets with a full scale printing machine, 4-colour sheet-fed offset printing press, and using a commercial printing ink. Hydrocyclone separated vessels according to their size and shape; the vessel-rich fraction had larger and more square-shaped vessels than the vessel-poor fraction. The vessel-rich pulps had a higher number of picks/cm² and also the picked area was larger than that of the feed pulps and the vessel-poor pulps. In the refining, the vessels were broken and split, and the bonding strength of the fibers was increased. Due to this, the refining of the vessel-rich fraction decreased the vessel picking tendency to the same or even lower level than that of the unfractionated pulp. Also the area of the pick marks decreased. This study proved that the method developed at KCL evaluates properly the vessel picking tendency of the various pulps. It was also shown that fractionation technique enables the study of pulps with various vessel contents: the chemical composition of those pulps, and the effect of separate treatment of those pulps on the vessel picking tendency. ▲

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Title	Applicability of fractionation of softwood and hardwood kraft pulp and utilisation of the fractions
Author(s)	Sari Asikainen
Abstract	<p>Fractionation of final or semi-finished fibres gives more advanced possibilities to design pulps with unique fibre characteristics. The objectives of this thesis were to clarify the applicability of fractionation of softwood and hardwood kraft pulp and utilisation of the fractions.</p> <p>Fractionation of softwood, birch and eucalyptus pulps gave fractions with substantially different physical and chemical properties. The contents of lignin, extractives and some metals were higher in the birch and softwood accept fraction because of the primary fines. Removal of primary fines from the oxygen-delignified birch kraft pulp gave a higher final brightness at slightly lower active chlorine consumption in DEDeD bleaching and improved brightness stability. When the birch fines were bleached using a ZeQP sequence, the extractives content of the fines fraction was reduced by 40%.</p> <p>The hydrocyclone- and pressure screen-fractionated softwood pulps were blended with thermomechanical (TMP) and groundwood (GW) pulp. The softwood long fibre fraction and the thick-walled fibre fraction gave in the mixture with mechanical pulp higher freeness values than the unfractionated pulp. The thick-walled fibre fraction gave clearly higher tear index values than the feed pulp in the mixture both with GW and TMP. Also, the long fibre fraction gave somewhat higher tear index values, especially when mixed with GW.</p> <p>Softwood thin- and thick-walled fibre fractions were refined separately. Fractions that were separately refined and after refining re-combined were then blended with GW. Separately refined fibre fractions in all cases gave higher freeness and higher fibre length of the chemical pulp-GW mixture than the unfractionated pulp-GW mixture. It was possible to increase the tear index by up to 16% and the fracture toughness index by up to 23% of the GW blend sheets by separate refining of the softwood kraft pulp fractions.</p> <p>Through hydrocyclone fractionation of birch pulp, a coarse fraction was obtained with a high tensile stiffness. The fine fraction had a high bonding ability. The coarse fraction could be used in the top layer of board or in fine paper. The fine fraction obtained by hydrocyclone and screen fractionation could be used for bonding in the middle layer of board making it possible to use coarser mechanical pulp.</p> <p>The vessel-picking tendency of eucalyptus pulp was significantly reduced by removing vessel elements from the pulp using hydrocyclone, and also by refining the vessel-rich fraction.</p>
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Nimeke	Fraktioiden soveltuvuus havu- ja lehtipuusulfaattimassalle ja fraktioiden hyödyntäminen
Tekijä(t)	Sari Asikainen
Tiivistelmä	<p>Kuituja voidaan räätälöidä fraktioimalla valmiita tai puolivalmiita kuituja. Tällöin saadaan kuituja, joilla on ainutlaatuiset ominaisuudet. Työn tavoitteena oli selvittää fraktioiden soveltuvuutta havu- ja lehtipuusulfaattimassoille. Lisäksi mietittiin fraktioiden hyötykäyttöä.</p> <p>Fraktioimalla havu-, koivu- ja eukalyptusmassaa saatiin kaksi fraktiota, jotka poikkesivat toisistaan sekä fysikaalisilta että kemiallisilta ominaisuuksiltaan. Havu- ja koivumassan akseptissa oli suurempi ligniini-, uuteaine- ja metallipitoisuus kuin rejektissä, mikä johtuu suuremmasta primäärisen hienoaineen määrästä. Kun happidelignifioidusta koivumassasta erotettiin primäärinen hienoaine, aktiivikloorin kulutus väheni DEDeD-sekvenssissä. Massan loppuvaaleus oli suurempi ja vaaleuden pysyvyys parempi kuin fraktioimattomalla massalla. Koivumassan hienoainefraktioiden uuteainepitoisuutta voitiin pienentää 40 % valkaisemalla se ZeQP-sekvenssillä.</p> <p>Painesihteilä ja pyörrepuhdistimella saadut havumassan kuitufraktiot seostettiin hierteen ja hiokkeen kanssa. Kun havupuun paksuseinämäinen tai pitkäkuituinen jae seostettiin hiokkeen kanssa, seoksella oli merkittävästi suurempi freeness kuin fraktioimattoman massan ja hiokkeen seoksella. Paksuseinämäinen jae seostettuna joko hierteen tai hiokkeen kanssa antoi selkeästi suuremman repäisylujuuden kuin fraktioimaton massa seoksessa. Myös pitkäkuitujae seoksessa, erityisesti hiokkeen kanssa, paransi seoksen repäisylujuutta. Pyörrepuhdistimella fraktioidun havumassan fraktioille tehtiin erillisjauhatusta. Kun erillään jauhetut ja jauhatuksen jälkeen yhdistetyt fraktiot seostettiin hiokkeen kanssa, oli seoksella suurempi freeness ja kuidunpituus kuin fraktioimattoman massan ja hiokkeen seoksella. Jauhamalla fraktiot erillään ja yhdistämällä ne jauhatuksen jälkeen oli mahdollista parantaa seoksen repäisylujuutta 16 % ja murtositkeyttä 23 %.</p> <p>Fraktioimalla koivumassa pyörrepuhdistimella saatiin karkea jae, jolla oli hyvä vetojäykkyys. Vastaavalla hienofraktiolla oli hyvä sitoutumiskyky. Karkeafraktiota voitaisiin käyttää joko kartongin pintakerroksessa tai hienopaperissa. Hienoajetta voitaisiin käyttää kartongin keskikerroksessa parantamaan sitoutumista, jolloin olisi mahdollista käyttää karkeampaa mekaanista massaa.</p> <p>Eukalyptusmassan nukkautumisherkkyttä voitiin vähentää pyörrepuhdistamalla putkiloita eukalyptusmassasta ja putkilorikkaan jakeen jauhatuksella.</p>
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