On the potential utilisation of sawdust and wood chip screenings

Risto Korpinen

Laboratory of Fibre and Cellulose Technology
Department of Chemical Engineering
Åbo Akademi University

Turku/Åbo 2010

On the potential utilisation of sawdust and wood chip screenings

Risto Korpinen

Laboratory of Fibre and Cellulose Technology
Department of Chemical Engineering
Åbo Akademi University

Turku/Åbo 2010

Preface

This thesis is a summary of the following publications, referred to the text with the corresponding Roman numerals. Also unpublished data are included.

I.   Korpinen, R.I., Hultholm, T.E.M., Lönnberg, B.K., Fardim, P.E. (2008) Black liquor impregnation of Scots pine sawdust and chip screenings. Appita Journal 61(3): 220–227.

II.   Korpinen, R., Hultholm, T., Lönnberg, B, Achrén, S. (2006) Development of sawdust cooking. Appita Journal 59(5): 406–411.

III. Korpinen, R., Fardim, P. (2009) Lignin extraction from wood biomass by a hydrotropic solution. O Papel 70(5): 69–82.

IV.   Korpinen, R., Fardim, P. (2008) Wood chip screenings as a source of energy, kraft pulp and functional chemicals: a Nordic perspective. O Papel 69(5): 56–73.

V.   Korpinen, R.I., Fardim, P.E. (2009) Reinforcement potential of bleached sawdust kraft pulp in different mechanical pulp furnishes. BioResources 4(4): 1572–1585.

Supporting publications

1. Korpinen, R., Hultholm, T., Lönnberg, B., Achrén, S. (2005) Development of sawdust cooking. In: Proceedings of the 59th Appita Annual Conference and Exhibition, Vol. 1, Auckland, New Zeeland. pp. 453–459.

2. Korpinen, R., Fardim, P. (2006) Characterisation of sawdust-like wood materials. In: Proceedings of the 9th European Workshop on Lignocellulosics and Pulp, Vienna, Austria. pp. 315–318.

3. Korpinen, R., Hultholm, T., Lönnberg, B., Fardim, P. (2007) Impregnation of finely divided wood materials from Scots pine (Peer reviewed). In: Proceedings of the 61st Appita Annual Conference and Exhibition, Gold Coast, Australia. pp. 53–61.

4. Lindström, N., Korpinen, R., Fardim, P. (2008) Surface chemistry and spatial distribution of polysaccharides and lignin in kraft pulps as investigated by XPS, ToF-SIMS and Py-GC/MS. In: Proceedings of the 10th European Workshop on Lignocellulosics and Pulp, Stockholm, Sweden. pp. 5–8.

Table of contents

Table of figures

List of tables

List of abbreviations, acronyms and symbols

a	annum
admt	air-dried metric tonne
ADt	air-dried tonne
AQ	anthraquinone
Ara	arabinose
ASE	accelerated solvent extraction
b	bark content
bar	bar, 10^5 Pa
BC	birch chips
BCS	birch chip screenings
BSDKP	bleached sawdust kraft pulp
c	centi-, 10^{-2}
c	concentration
CA	California
CED	copper ethylenediamine
CPPA	The Canadian Pulp and Paper Association
CTMP	chemithermomechanical pulp
D	chlorine dioxide stage
DC	District of Columbia
D.S.	dry solids
EA	effective alkali
FCT	Fiber- och cellulosateknologi (Fibre and Cellulose Technology)
E_O	alkaline extraction stage with oxygen addition
E_P	alkaline extraction stage with hydrogen peroxide addition
FL	Florida
FT-IR	Fourier transform infrared spectroscopy
g	acceleration of gravity, 9.80665 m/s^2
g	gram
G	giga-, 10^9
GA	Georgia
Gal	galactose
GalA	galacturonic acid

GC	gas chromatography
Glc	glucose
GlcA	glucuronic acid
Gu	guaiacyl lignin
h	hour
HBL	hot black liquor
HMDS	hexamethyldisilazane
HP	high pressure
HW	hardwood
IDE	Impregnation, Depolymerisation, Extraction- pulping concept
INBAR	International Network for Bamboo and Rattan
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
J	Joule
k	kilo-, 10^3
KTT	Kemisk träförädlingsteknik (Pulping Technology)
l	litre
LHV	low heating value
m	mass
m	milli-, 10^{-3}, metre
M	molar, mol/l, mega-, 10^6
M&D	Messing-Durkee
m^3/admt	solid cubic metre per air-dry metric tonne of pulp
m^3/sob	solid cubic metre over bark
m^3/sub	solid cubic meter under bark
Man	mannose
min	minute
MHC	minimum hydrotrope concentration
mol	mole
n	amount of substance
NY	New York
O	oxygen delignification stage

OECD	Organisation for Economic Cooperation and Development
o.d.	oven-dry
Pa	Pascal
PaPSaT	International Doctoral Programme in Pulp and Paper Science and Technology
PC	pine chips
PCS	pine chip screenings
PFI	Papirindustriens Forskningsinstitutt (The Norwegian Pulp and Paper Research Institute)
PGW	pressurised groundwood
PS	polysulphide
PSD	pine sawdust
PTS	Papiertechnische Stiftung
Rha	rhamnose
RIF	reinforcement fibre
RMP	refiner mechanical pulp
s	second
SC	spruce chips
SCAN	Scandinavian Pulp, Paper and Board Testing Committee
SIDS	Screening Information Data Set
S/PCS	spruce/pine chip screenings
SSD	spruce sawdust
SSF	simultaneous saccharification and fermentation
SW	softwood
Sy	syringyl lignin
SXS	sodium xylenesulphonate
t	tonne, 1000 kg
TAPPI	Technical Association of the Pulp and Paper Industry
TMCS	trimethylchlorosilane
TMP	thermomechanical pulp
TOC	total organic carbon
UK	United Kingdom
UNEP	United Nations Environment Programme

UPM	United Paper Mills
USA	United Stated of America
UV	ultraviolet
V	volume
VMR	Virkesmätningsrådet (The Swedish Timber Measurement Council)
VTT	Valtion teknillinen tutkimuskeskus (Technical Research Centre of Finland)
w	weight
W_{cons}	wood consumption
WL	white liquor
$X_{D.S.}$	black liquor dry solids content
Xyl	xylose
Y	yield
γ-butyrolactone	gamma-butyrolactone
μ	micro-, 10^{-6}
ρ	density
4-*O*-Me-GlcA	4-*O*-methyl-glucuronic acid
°C	degree Celsius, centigrade
°SR	Schopper-Riegler freeness

Abstract

Risto Korpinen: *On the potential utilisation of sawdust and wood chip screenings*

Doctor of Science in Technology Thesis, Åbo Akademi University, Department of Chemical Engineering, Turku 2010, 84 pages, 26 figures and 26 tables.

The work was carried out under supervision of Professor Bruno Lönnberg and Professor Pedro Fardim at the Laboratory of Fibre and Cellulose Technology, Åbo Akademi University.

Keywords: *Sawdust, wood chip screenings, black liquor impregnation, sawdust cooking, hydrotropic extraction, energy, ethanol, chemicals, reinforcement fibre pulp*

This work is based on the utilisation of sawdust and wood chip screenings for different purposes. A substantial amount of these by-products are readily available in the Finnish forest industry.

A black liquor impregnation study showed that sawdust-like wood material behaves differently from normal chips. Furthermore, the fractionation and removal of the smallest size fractions did not have a significant effect on the impregnation of sawdust-like wood material.

Sawdust kraft cooking equipped with an impregnation stage increases the cooking yield and decreases the lignin content of the produced pulp. Impregnation also increases viscosity of the pulp and decreases chlorine dioxide consumption in bleaching. In addition, impregnation increases certain pulp properties after refining.

Hydrotropic extraction showed that more lignin can be extracted from hardwood than softwood. However, the particle size had a major influence on the lignin extraction. It was possible to extract more lignin from spruce sawdust than spruce chips.

Wood chip screenings are usually combusted to generate energy. They can also be used in the production of kraft pulp, ethanol and chemicals. It is not economical to produce ethanol from wood chip screenings because of the expensive wood material. Instead, they should be used for production of steam and energy, kraft pulp and higher value added chemicals.

Bleached sawdust kraft pulp can be used to replace softwood kraft pulp in mechanical pulp based papers because it can improve certain physical properties. It is economically more feasible to use bleached sawdust kraft pulp in stead of softwood kraft pulp, especially when the reinforcement power requirement is moderate.

Sammandrag

Denna avhandling baserar sig på olika sätt att utnyttja sågspån och finspån. Stora mängder av dessa biprodukter bildas inom den finska skogsindustrin och tillgången är god.

Genom att studera svartlutsimpregnering av spån och flis var det möjligt att konstatera att spånaktigt vedmaterial uppför sig annorlunda än normal flis. Dessutom påverkade fraktionering och avlägsning av de mest finfördelade fraktionerna inte märkbart impregneringen.

Studien har visat att sågspånskok försett med ett förimpregneringssteg höjer massans utbyte och minskar massans ligninhalt efter koket. Ett förimpregneringssteg ökar också massans viskositet och minskar klordioxidförbrukningen vid blekningen. Dessutom förbättras massans vissa fysikaliska egenskaper.

Hydrotropisk extraktion visade att det är möjligt att extrahera mera lignin från lövved än barrved. Vedmaterialets partikelstorlek spelade dock en betydande roll, mera lignin kunde extraheras från gransågspån än granflis.

Finspån bränns vanligen för energiåtervinning. Det kan även användas för produktion av sågspånsmassa, etanol och kemikalier. Studien har visat att etanolproduktion inte är lönsam eftersom vedmaterialet är dyrt. Spån borde istället omvandlas till energi och ånga, sågspånsmassa eller kemikalier med högre förädlingsvärde.

Långfibrig barrvedsmassa kan ersättas med blekt sågspånsmassa för att förbättra vissa egenskaper hos mekaniska massor. Användningen av sågspånsmassa är ekonomiskt mera lönsamt än bruket av barrvedsmassa om armeringsbehovet är rimligt.

Tiivistelmä

Risto Korpinen: *On the potential utilisation of sawdust and wood chip screenings*

Väitöskirja, Åbo Akademi, Kemiantekniikan laitos, Turku 2010, 84 sivua, 26 kuvaa ja 26 taulukkoa.

Väitöstyön ohjasivat professori Bruno Lönnberg ja professori Pedro Fardim Åbo Akademin Kuitu- ja selluloosateknologian laboratoriosta.

Avainsanat: *Sawdust, wood chip screenings, black liquor impregnation, sawdust cooking, hydrotropic extraction, energy, ethanol, chemicals, reinforcement fibre pulp*

Väitöskirja perustuu metsäteollisuuden hienojakoisten sivutuotteiden hyödyntämiseen. Sivutuotteita, kuten sahan- ja seulontapurua, syntyy Suomen metsäteollisuudessa runsaasti ja niitä on helposti saatavilla.

Mustalipeäimeytyskokeiden perusteella voitiin todeta, että purumainen puuaines käyttäytyy eri tavalla kuin normaali hake. Lisäksi purun fraktioinnilla ja hienojakoisimpien fraktioiden poistolla ei ollut suurta vaikutusta imeytykseen.

Imeytysvaiheella varustettu purukeitto lisää keitonjälkeistä saantoa ja vähentää sellun ligniinipitoisuutta. Imeytysvaihe lisää myös sellun viskositeettia ja vähentää klooridioksidin kulutusta valkaisussa. Lisäksi valkaisun jälkeinen jauhatus osoitti, että imeytysvaihe parantaa sellun tiettyjä fysikaalisia ominaisuuksia.

Hydrotrooppinen uutto osoitti, että lehtipuusta voidaan uuttaa enemmän ligniiniä kuin havupuusta. Kuitenkin puuaineen raekoolla oli merkittävä vaikutus ligniinin uuttoon. Kuusisahapurusta saadaan uuttamalla enemmän ligniiniä kuin kuusihakkeesta.

Seulontapuru poltetaan yleensä energiaksi. Sitä voidaan käyttää myös purusellun, etanolin ja kemikaalien valmistukseen. Etanolin valmistus ei ole kannattavaa puuraaka-aineen kalleuden vuoksi. Puru kannattaa mieluummin muuttaa energiaksi ja höyryksi, puruselluksi tai korkean jalostusarvon kemikaaleiksi.

Valkaistua purusellua voidaan käyttää pitkäkuituisen havusellun sijaan parantamaan mekaanisten massojen tiettyjä ominaisuuksia. Purusellun käyttö on taloudellisesti kannattavampaa kuin havusellun käyttö armeeraustarpeen ollessa kohtuullinen.

1 Introduction

Sawdust is a by-product from sawmills. Wood chip screenings, is in this thesis, are defined as finely divided wood material which has passed through the screens when wood chips were screened prior to pulping, *i.e.* wood material smaller than the accepted size for chips.

The quality of sawdust depends on the saw type, method of sawing, type of tree used, and the storage method of logs including temperature, moisture and season. Meanwhile the factors which affect the properties of chip screenings are *e.g.* chipper type, debarking method, the storage method of chips, screen type, season and temperature (Isomäki 1970; Rantasuo 1976; Liiri 1979). Thus, sawdust and chip screenings from different mills can be very heterogeneous raw materials.

The aim of this work is the utilisation of sawdust and wood chip screening for different purposes. A significant annual amount of these by-products are formed and available in the Finnish forest cluster.

1.1 Sawdust

Approximately half of the log volume can be converted into timber during a sawing process, as seen in Figure 1. The rest of the log volume is converted into chips, sawdust and bark.
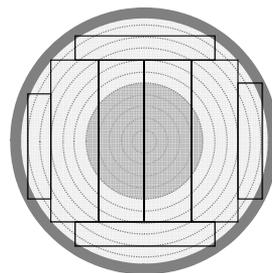
2.2 solid m³ log

1.0 solid m³ timber
0.7 solid m³ chips
0.3 solid m³ sawdust
0.2 solid m³ bark

Figure 1. Material formed during sawing process, redrawn from Martikainen 2002.

The production of sawn softwood in Finland during 2000–2008 is illustrated in Table 1. The amount of chips, sawdust and bark is calculated using the data in Figure 1.

Table 1. The formation of various product fractions (10^6 solid m^3) from sawn softwood in Finland during 2000–2008 (Finnish Forest Industries Federation 2009).

Year	Timber	Chips	Sawdust	Bark
2000	13.32	9.32	4.00	2.66
2001	12.67	8.87	3.80	2.53
2002	13.28	9.30	3.98	2.66
2003	13.65	9.55	4.09	2.73
2004	13.46	9.42	4.04	2.69
2005	12.19	8.53	3.66	2.44
2006	12.15	8.50	3.64	2.43
2007	12.40	8.68	3.72	2.48
2008	9.80	6.86	2.94	1.96

The production of sawn softwood, *i.e.* timber has varied between 9.80 and 13.65 million solid m^3. This means that the forest industry has created 2.94–4.09 million solid m^3 sawdust.

The quality of sawdust is mainly dependent on the particle size of sawdust. The particle size of sawdust is not uniform and the distribution is usually concentrated on the smallest size fractions (Isotalo et al. 1964a; Surewicz 1974; Bublitz and Yang 1975; Taylor 1977; Joshi et al. 1982; MacLeod and Kingsland 1990; Korpinen and Fardim 2006; Bergström et al. 2008). However, there may be some difficulties comparing the different studies due to the different fractionation processes. The fibre length is greatly affected by the particle size of the wood material. The average length of softwood fibres is about 3 mm, whereas the average fibre length of softwood sawdust is approximately 1.0–1.2 mm (Isotalo et al. 1964a; Uusvaara 1975; Arends and Donkersloot-Shouq 1985; Korpinen 2002). The shortening of the fibre length is due to the cutting that appears in sawing (Bausch and Hartler 1960).

Bark that exists in sawdust is harmful, especially when sawdust is used in the production of kraft pulp. Bark consumes cooking chemicals, causes discolouring and impairs the quality of pulp. In addition, the cooking yield of bark is low (Uusvaara 1975). It has been

found that Scots pine sawdust contained 0.4% bark in summer, 1.3% in winter and the annual mean bark content was 0.7%. It has also been found that Norway spruce contained 0.5% bark in summer, 2.7% in winter and the annual mean bark content of Norway spruce sawdust was 1.3% (Uusvaara 1975).

Sawdust originates normally from older parts of the tree stem. Sawlogs typically represent a diameter exceeding 150 mm, as pulpwood logs have an acceptable diameter of around 70 mm (Lukkari 1998). Subsequently, sawdust may contain a larger proportion of heartwood. Juvenile wood including heartwood compared to mature wood has shorter and narrower cells, thinner cell walls, higher earlywood/latewood ratio, lower cellulose content, higher hemicellulose content, higher lignin content and higher extractives content (Mimms et al. 1995; Parham 1983b; Zobel and Sprague 1998).

1.2 Chip screenings

Debarked logs are cut into smaller pieces of relatively uniform chip size before they are processed into pulp. The ideal chip length is 10–30 mm and chip thickness 2–5 mm (Mimms et al. 1995; Ressel 2006). During the chipping process oversize and undersize fractions are also formed and they must be removed by screening because these fractions will reduce the pulp quality and they may complicate digester operations (Fuller 1983). The oversize fraction is reprocessed by rechipping, slicing or crushing and is sent back to the accept chip flow (Koskinen 1999). The undersize fraction, *i.e.* wood chip screenings, is usually combusted to generate heat and steam but it can further be used as a raw material for kraft pulping (Mimms et al. 1995). Chip screenings may also be used in biorefineries to produce functional chemicals, fibres, fuels, energy and other industrial products instead of combusting them.

The softwood consumption in cooking usually ranges from 5.1–5.5 m^3sub/ADt (solid cubic metre under bark per air-dry tonne of pulp) (Svedman et al. 1998; Fogelholm and Suutela 2000; Axegård et al. 2002). The wood loss in chip screening varies from 1% up to 3% (Fuller 1983; Pellikka and Saviharju 1983; Fogelholm and Suutela 2000), hence the amount of wood material not entering the digester

due to screening loss is 0.051–0.170 m³sub/ADt or 20.4–68.0 o.d. kg/ADt when the basic density of wood is 400 kg/m³ and dry content 50% (Duchesne et al. 1997). In comparison, a pulp mill that produces bleached kraft pulp from *Eucalyptus grandis* wood, the screening loss ranges from 0.039–0.133 m³sub/ADt (17.7–59.8 o.d. kg/ADt) when the basic wood density is 450 kg/m³ (Backman and de Leon 1998; Dhamodaran and Gnanaharan 2006) and the wood consumption in cooking is 3.89–4.30 m³sub/ADt (Backman and de Leon 1998; Grattapaglia 2007).

The production of different kraft pulps in Finland 2000–2007 is presented in Table 2.

Table 2. Production of kraft pulp (10⁶ tonnes) in Finland 2000–2007 (Aarne 2008).

Year	Bleached softwood	Bleached hardwood	Unbleached
2000	3.50	2.90	0.71
2001	3.28	2.62	0.64
2002	3.55	2.90	0.69
2003	3.76	2.93	0.66
2004	3.96	3.15	0.67
2005	3.47	2.78	0.53
2006	4.11	3.20	0.64
2007	4.18	2.92	0.60

The generation of softwood chip screenings can be calculated using the previous data. It has varied between 0.17–0.22 million solid m³ with low screening loss and 0.56–0.71 million solid m³ with high screening loss.

It can be seen in Tables 1 and 2 that there is a substantial amount of finely divided lignocellulosic raw material that can be used for several purposes.

1.3 Impregnation of wood material by black liquor

The purpose of the impregnation for pulping is to transport the active chemicals into the wood structure. The impregnation process can be divided into two different stages, *i.e.* penetration and diffusion. In the penetration stage the impregnation liquor flows into and through the pores of the wood. During diffusion, active chemicals move from a

high concentration area to a low concentration area, namely from the liquor to the wood structure (Virkola et al. 1983; Mimms et al. 1995). There are factors related to the liquor and wood which influence the impregnation. Factors related to the impregnation liquor are pressure, temperature, pH, concentration, surface tension and viscosity, as those related to the wood material are the type of wood, the chip dimensions, the moisture content, the air content and the capillary structure (Stone and Förderreuther 1956).

Hardwood is denser than softwood but it is easier to penetrate, because it contains vessel elements which have a large diameter. The penetration in hardwood is very small across the grain because its pit membranes are not very porous, which retards the introduction of liquor into neighbouring cells (Clayton et al. 1989). Softwood does not contain vessel elements, and hence the penetration occurs mainly from lumen to lumen via the porous pits. In addition, the resin canals and rays conduct liquids in softwood (Matsumara et al. 1999). There are even internal differences in the wood itself. Springwood is easier to penetrate than summerwood because of the wider lumina and thinner, more perforated cell walls. Additionally, the sapwood penetrates faster than heartwood (Rydholm 1965; Ekman and Fogelberg 1966). While juvenile (resembling heartwood) has narrower cells, thinner cell walls, wider growth rings and a higher earlywood/latewood ratio than mature (sap)wood, heartwood is infiltrated and incrusted with organic extractives derived from stored starch, other sugars and fats. The extractives infiltrate fibre walls, plug vessels in hardwoods, incrust pit membranes and make penetration of wood by liquors difficult (Parham 1983b; Mimms et al. 1995; Zobel and Sprague 1998).

The moisture content of wood has a large effect on the impregnation. There is free water present in the wood cells, when the moisture content of the wood exceeds the fibre saturation point (Wiedenhoeft and Miller 2005). The concentration of the penetrating liquor approaches zero after 16 fibres (about 0.5 mm), if the wood moisture content is 45–50% in a theoretical case (Lönnberg et al. 1995). The moisture content has a definite influence on the void volume inside the fibres. Hence, due to its low moisture content, heartwood chips can take more impregnation liquor than sapwood chips, although they are more difficult to penetrate (Malkov et al. 2001).

Air inside the wood affects the penetration as well, because it prevents the impregnation liquor from penetrating into all voids in the chips. The commonly applied method to remove the air is pre-steaming, which improves the penetration (Aurell et al. 1958). The required steaming time is dependent on the wood. Air removal is faster from sapwood than from heartwood due to a removal or redistribution of resins during steaming. Even some changes of the bordered pit conditions provide a faster conduction (Matsumara et al. 1998; Matsumara et al. 1999; Malkov et al. 2002). In addition, an increased temperature or pressure would decrease the penetration time (Paranyi and Rabinovitch 1955; Woods 1956; Uhmeier 1997).

Increased pressure and reduced liquor viscosity due to a higher temperature also increase the penetration rate. The type of liquor influences the impregnation, *e.g.* it would be faster with black liquor than with white liquor or sodium hydroxide solution. This is probably a result of the black liquor compounds with surfactant characteristics (Robertsén et al. 1999). On the other hand, the black liquor would provide a slower penetration than white liquor, because of the large organic molecules present in the black liquor and its low surface tension would retard its permeability in the wood chips (Malkov 2002).

The diffusion rate of a liquid at low pH values is much faster in the longitudinal direction than in the radial or tangential directions of the wood chips. It has been claimed, that when the liquor pH is higher than 13, the diffusion rates tend to be nearly similar in all the main directions (Stone 1957). The chip thickness is the shortest dimension regarding the diffusion of cooking chemicals towards the chip centre (Hartler 1962). Although the chip thickness is a key dimension, the chip length also has a visible effect on the pulping results, *e.g.* the pulp yield, kappa number and effective alkali (EA) consumption (Akhtaruzzaman and Virkola 1979a; Akhtaruzzaman and Virkola 1979b).

The impregnation stage is usually considered to be finished in conventional kraft pulping, when the temperature has reached 140 °C, *i.e.* when the main delignification phase is initiated (Gullichsen 1999). The terminology, however, is not specifically agreed. The temperature may be raised even to 150 °C during the so-called initial delignification phase (Wilder and Daleski 1965). In some continuous

digester installations equipped with an impregnation zone, the temperature is here kept relatively constant at 115–130 °C for 45–60 min allowing chemical liquid to penetrate the chips and ions to diffuse from the exterior of the chips towards their centre as well as the fibre walls (Marcoccia et al. 1999).

1.4 Sawdust cooking

The production of sawdust kraft pulp was introduced in an industrial scale in the mid 1950's. Since the beginning the production has been carried out using continuous digesters.

Special techniques are required for the impregnation and cooking of sawdust. When the wood material comes into contact with a liquid, a compact sawdust matrix which is formed, has a tendency to limit the liquid flow through the material or perhaps prevent it almost totally. Sawdust is difficult or impossible to pulp in a conventional batch digester, because sufficient cooking is highly dependent on the liquor capability to circulate freely through the wood material. In addition, there is a problem of hang-ups in conventional continuous vertical digesters, *i.e.* there are interruptions of the free downward movement of the wood column inside the digester. Also, extraction screens are plugged (Markham 1984).

There are several digester systems suggested for sawdust pulping, *e.g.*, the Kamyr sawdust digester, IMPCO (ESCO) digester, Pandia digester and the Messing-Durkee (M&D) digester. The last mentioned is the most common method for the pulping of sawdust (Ingruber 1989). The M&D digester is shown in Figure 2 and Pandia digester in Figure 3.
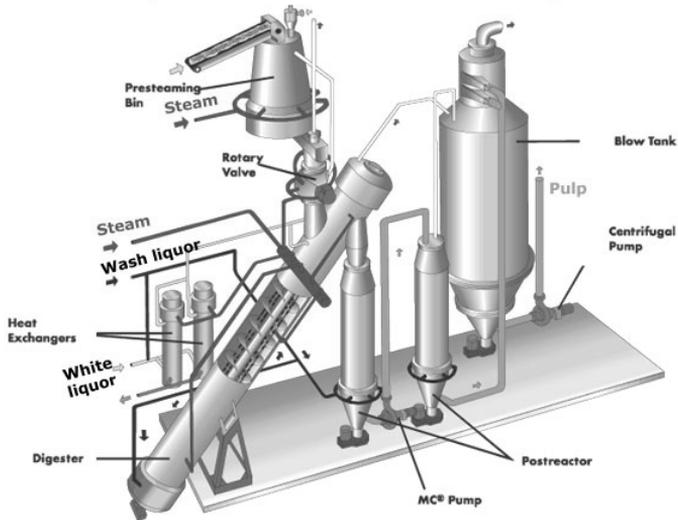
Figure 2. M&D digester. Andritz AG.
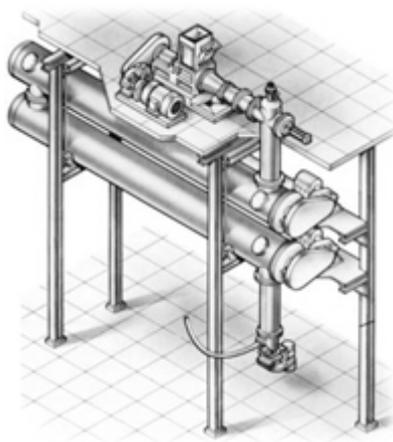
Figure 3. Pandia digester. GL&V Inc.

The M&D digester consists of a tube reactor with dome-shaped ends and the tube is inclined in a position of 45°. The tube is divided into an upper and lower compartment by a hollow midfeather. Sawdust is conveyed through the cooking liquor by a drag chain conveyor. The cooking liquor is heated in a heat-exchanger and added close to the entry of the sawdust, and the liquor-sawdust mixture is then brought to the cooking temperature by direct steam, because liquor displacement can hardly be done for separate heating. The cooking may also be extended in a post-reactor, which decreases the steam

consumption, levels the flow in the surge tube and increases the cooking volume (Liiri 1979).

The relatively short retention time is characteristic for an M&D digester due to the steam that occupies part of the digester volume and due to a limited mechanical conveyance. Installation of a larger conveyor to achieve a longer retention time would in fact be too expensive (Miele et al. 2001). The total cooking time, including the time in the digester and post-reactor, usually ranges from 15 to 30 min. The short retention time affects the cooking temperature and chemical consumption. The cooking temperature is kept normally at 170–185 °C, which corresponds to a pressure of 800–1050 kPa (8–10.5 bar), the alkali charge is 26–32% NaOH on o.d. wood and the liquor-to-wood ratio is 4:1–5:1 (Rantasuo 1976; Virkola et al. 1983). The M&D sawdust digester system of Pietarsaari pulp mill installed 2004 starts with an impregnation stage performed at a low temperature and the cooking is finished in a separate digester (Anon. 2004). The production capacity of Pietarsaari sawdust plant is 40 000 tonnes per annum (Graeme 2004).

The pulping yield of sawdust is usually lower compared to pulping of chips. The yield difference for sawdust varies between 2.1–2.7%. The particle size of sawdust affects the yield, especially the amount of wood flour in sawdust (Bail 1979). The lower yield of sawdust pulping can be improved by addition of, *e.g.*, anthraquinone (AQ) or polysulphide (PS) (Virkola 1980; Virkola 1981; Pekkala 1982; MacLeod and Kingsland 1990; Vuorinen 1993).

1.5 Hydrotropic extraction of lignin

Hydrotropic solutions are aqueous salt solutions which improve the solubility of slightly soluble substances (*e.g.*, lignin) in comparison with pure water at the same temperature (Andelin et al. 1989). Typical near-saturated hydrotropic salt solutions are prepared from alkali or alkaline earth salts of benzoic acid, salicylic acid, xylenesulphonic acid, cymenesulphonic acid, benzenesulphonic acid, phenolsulphonic acid, toluenesulphonic acid and naphthalenesulphonic acid (McKee 1943; Traynard 1955). The chemical structures of these sodium salts can be seen in Figure 4.
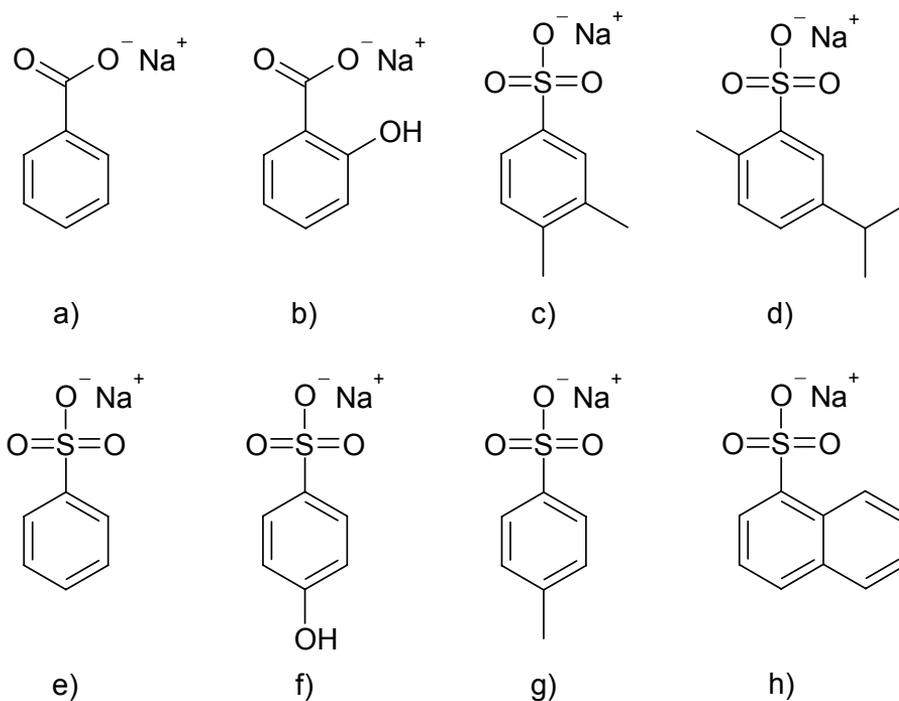
Figure 4. Hydrotropic sodium salts: a) sodium benzoate, b) sodium salicylate, c) sodium xylenesulphonate, d) sodium cymenesulphonate, e) sodium benzenesulphonate, f) sodium phenolsulphonate, g) sodium toluenesulphonate and h) sodium naphthalenesulphonate. Only one isomer of the all possible isomers is shown.

The structure of hydrotropic compounds is similar to those of surfactants, *i.e.* they are amphiphilic substances composed of both a hydrophilic and a hydrophobic functional group. Short-chain hydrotropic compounds have, however, a weaker hydrotropic character than surfactants (Varade and Bahadur 2004). The hydrotropic compounds are able to increase the solubility of organic compounds in water. This ability is usually the strongest when the hydrotropic compound concentration is high enough to form associated structures. The concentration at which self association begins is defined as the minimum hydrotrope concentration (MHC). Relatively high concentrations of hydrotropic compounds are required to reach the MHC.

The value of MHC for sodium xylenesulphonate is 0.38–0.40 M (Balasubramanian et al. 1989; Varade and Bahadur 2004). Hydrotropic

compounds are different from surfactants because their hydrophobicity is not sufficient enough to create well organised self-associated structures, such as micelles, even well above the MHC (Hodgdon and Kaler 2007). Instead, hydrotropes form two-dimensional layered sandwich type structures (Srinivas 1997). Relatively high concentrations of hydrotropic compound are required to initialise solubilisation and the maximum amount that solubilises into the aqueous hydrotrope solution is high compared with what is found in an aqueous micellar solution of a surfactant (Friberg and Brancewicz 1997).

The most generally used hydrotropic compound for the recovery of cellulose and lignin from lignocellulosic material is sodium xylenesulphonate because it is an effective solvent. When the lignocellulosic material is extracted with approximately neutral 30–40% (w/w) solution of sodium xylenesulphonate, the same solution can be used for six or seven times before recovered for re-use. During extraction the hydrotropic solution becomes more enriched with lignin and the solution becomes more effective as solvent for lignin. The limit for re-using the solution is reached when saturation with lignin is approached (about 350 grams per litre of solution) (McKee 1943; McKee 1946).

Typically the lignocellulosic material is treated at 150 °C for 11–12 hours. After the finished extraction, the pulp needs to be washed with fresh solution of hydrotropic solution because lignin has tendency to precipitate on the fibres during washing of the pulp with water. Thereafter the pulp can be washed with water (McKee 1943; Traynard 1955; Traynard and Eymery 1955; Gordon at al. 1997). It has been stated that the hydrotropic extraction process is not suited for softwoods (Hägglund 1951; Andelin et al. 1989) because softwoods contain more chemically resistant guaiacyl (Gu) lignin in comparison with hardwoods which contain less resistant syringyl (Sy) lignin. The Sy/Gu ratio among different hardwoods varies from 2:1 to 4:1 (Adler 1977; Parham 1983a).

The recovery of the hydrotropic solution is uncomplicated. The concentration of the solution is reduced from 30% or 40% to 10% adding water. The lignin is precipitated and can be filtered off from the solution. The filtrate then is evaporated to the original 30–40% concentration. The recovered solution is as effective as the original

solution. The same solution has been used for 72 subsequent laboratory experiments with no decrease in effectiveness (McKee 1946). The accumulated impurities can be purified from the solution by adding 1 part by weight Ca(OH)$_2$ to 200 parts by weight of the solution. The precipitated impurities can be then filtered off from the solution (McKee 1943).

The sodium xylenesulphonate solution is nonscaling and noncorrosive and free from unpleasant odour (Dhamodaran et al. 2003). Sodium xylenesulphonate has low volatility with a vapour pressure of <2.0 10^{-5} Pa at 25 °C in comparison with water (3.2·10^3 Pa at 25 °C) or ethanol (7.9·10^3 Pa at 25 °C). Further, studies across the hydrotropes category show rapid and complete biodegradation under aerobic conditions and the hydrotropes are considered to be readily biodegradable according to OECD criteria (UNEP 2005).

1.6 Energy, kraft pulp and chemicals from wood chip screenings

Like stated earlier, wood chip screenings are usually combusted to generate steam and heat or used in kraft pulp production. Chip screenings may also be used in biorefineries to produce functional chemicals, fibres, fuels, energy and other industrial products. The biorefinery concept can be divided into two major paths which are illustrated in Figure 5.
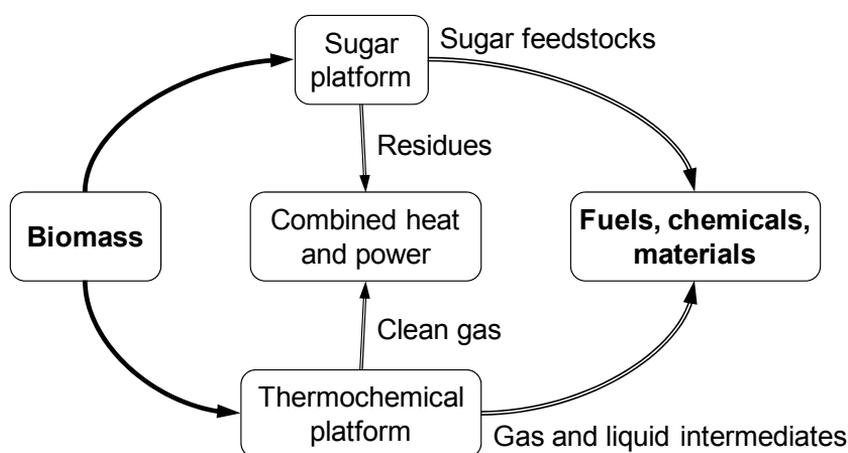
Figure 5. Biorefinery concept, redrawn from Crocker and Crofcheck 2006.

The sugar platform consists of conversion of biomass into sugar components by means of chemical and biological methods. The aim is to produce low-cost sugar feedstocks for production of fuels, chemicals and other materials. The residues from the sugar platform can be used for power generation or for production of other products. The purpose of the thermochemical platform is to convert biomass and/or biorefinery residues to pyrolysis oil and syngas. The obtained gas and liquid intermediates can be used as raw fuels or further processed to fuels and chemicals (Crocker and Crofcheck 2006). The biorefinery process includes gasification to produce syngas, thermochemical liquefaction and/or pyrolysis for bio oils production, anaerobic digestion for biogas production and hydrolysis of carbohydrates using mineral acids, bases, supercritical fluids and enzymes. These products are then further processed to: alkanes by Fischer-Tropsch synthesis from syngas, methanol and various derivatives from syngas, liquid alkane fuels from liquefaction and pyrolysis, aromatic carbohydrates from sugars and methanol and ethanol from fermentation of sugars (Hamelinck and Faaij 2006; Huber and Dumesic 2006; Ragauskas et al. 2006; Kamm 2007), see Figure 6.
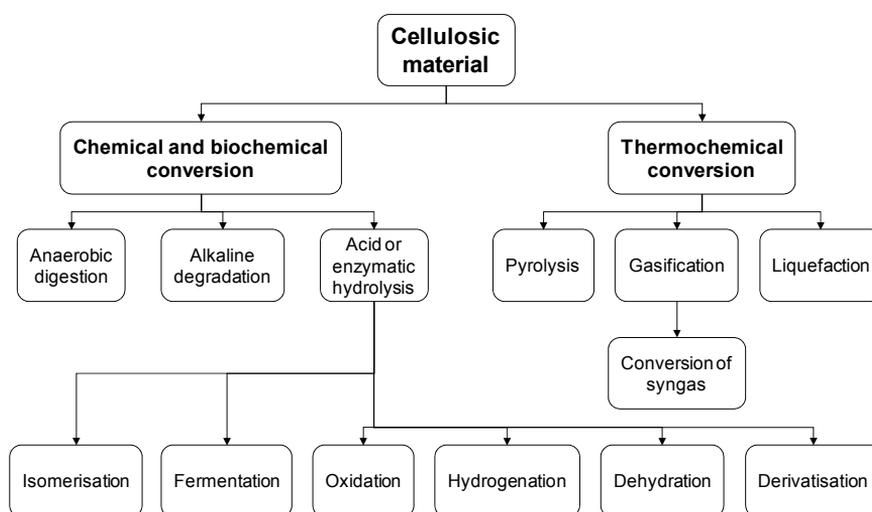
Figure 6. Conversion of cellulosic materials, redrawn from Alén 1990.

1.7 Properties of sawdust kraft pulp

When comparing pulps made of sawdust or chips, both from the same wood, it has been found that the strength properties of sawdust pulp are lower. Up to 30% sawdust pulp can be mixed with conventional softwood or hardwood pulp before strength properties start to impair. Usually sawdust pulp is comparable with hardwood pulps (Isotalo et al. 1964a; Isotalo et al 1964b; Irvine 1966; Procter and Chow 1976; Taylor 1977; Liiri 1979; Arends and Donkersloot-Shouq 1985).

Sawdust pulp has good absorption capacity, opacity, porosity and low extractive content. The strength properties of sawdust pulp compared to conventional chip pulps can be seen in Figure 7.
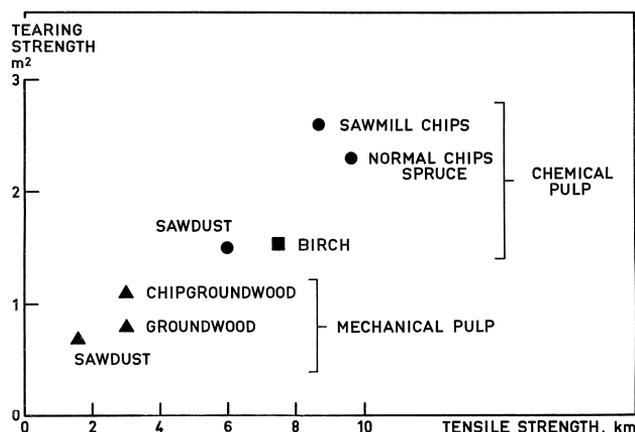
Figure 7. Strength properties of different pulps (Lönnberg 1971).

The brightness of bleached sawdust kraft pulp decreases less during refining than the brightness of bleached softwood chip kraft pulp. Papermakers can therefore save expensive brightening agents (Taylor 1977). Sawdust pulp has good bulk [Paper V] which increases opacity and light scattering of pulp. Increased opacity and light scattering in turn increase brightness (Häggblom-Ahnger and Komulainen 2001). Also, the opacity of the bleached sawdust pulp remains higher during refining compared to a corresponding chip pulp (Isotalo et al. 1964).

Adding sawdust pulp into long fibre pulps, despite of the lower strength properties of sawdust pulp compared to chip pulps, certain significant benefits are achieved. Sawdust pulp improves water removal and formation of paper in the paper machine due to low

flocking tendency. Short fibres improve opacity, surface smoothness, absorbency, dimension stability and printability (Rantasuo 1976; Liiri 1979).

A main area of utilisation of sawdust pulp is laminated papers. Sawdust pulp can also be used in kraft paper, sack paper, board, filter paper, blotting paper, tissue, copy paper, printing paper, top liner board, grease-proof and glassine (Taylor 1977; Bail 1979; Liiri 1979, Graeme 1997).

2 Materials and methods

2.1 Black liquor impregnation [I]

Scots pine (*Pinus sylvestris*) chips and Scots pine chip screenings were collected at a pulp mill in southwestern Finland. The bark of the initial pine logs at the mill was softened in a heating chamber (bark temperature was maintained at least at 15 °C) and the logs were debarked in a dry debarking drum. The debarked logs were chipped by a Rauma GS 15-3300 disc chipper, 3 300 mm in diameter and applied with 15 knives. The chips were stored in a pile and screened with a disc screen. The wood raw material that passed through the disc screen was re-screened with a vibratory chip screen, and the particles that passed through 6.5 mm openings in diameter were regarded as chip screenings and were stored outdoors. The two chip piles at the mill contained mill produced pine chips and pine sawmill chips, respectively. The test chips were taken from the pile containing mill produced pine chips, and the chip screenings were obtained from a furnish containing 80% mill produced chips and 20% sawmill chips. Mill produced chips and sawmill chips were mixed before screening and pulping at the pulp mill. The wood procurement area of the pulp mill and sawmill which provided sawmill chips consisted of southern and western Finland.

Scots pine sawdust was collected from a sawmill in south-western Finland and the wood procurement area consisted of south-western Finland. The saw logs were stored on land without water sprinkling and they were sawn undebarked and without heating by application of a chipping canter, a circular saw and a band saw. The sawdust generated was stored in the open air.

The sampled pine chip screenings, sawdust and chips were air-dried. The sawdust and chip screenings were first fractionated by a Williams chip thickness screen, see Figure 8.

Figure 8. Fractionation procedure of Scots pine sawdust and chip screenings.

The slots of the respective screens were 6, 4 and 2 mm wide. The fractionation time was 5 min and the visible bark particles were removed by hand-picking. Then the wood particles which passed through the entire screen set were further fractionated by application of an Endecotts laboratory test sieve. The square openings of the separate sieves were 1x1, 0.5x0.5 and 0.25x0.25 mm², and now the fractionation was conducted for 10 min. Hence, the screening and sieving fractions obtained were as follows: <0.25 mm, 0.25–0.5 mm, 0.5–1 mm, 1–2 mm, 2–4 mm, 4–6 mm and >6 mm, and their proportions were given as a percentage of the total sample weight.

The chip screenings and sawdust were distributed over the fractions examined, as given in Table 3, and the total amount of the wood raw material was kept constant. Pine chip screenings has a more homogeneous composition than sawdust containing less fine and large wood particles, which may complicate the interpretation of the impregnation. In addition, bark content of sawdust and chip screenings was different and sawdust contained more bark that was able to be removed by hand-picking.

Table 3. Distribution of the pine chip screenings (PCS, upper table) and the pine sawdust (PSD, lower table) in the fractions examined *)

Furnish	Bark	<0.25 mm	0.25–0.5 mm	0.5–1 mm	1–2 mm	2–4 mm	4–6 mm	>6 mm	Sum
	f_A	f_B	f_C	f_D	f_E	f_F	f_G	f_H	Σf_{A-H}
	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(g)
PCS-A	94.8	995.5	3493.5	11681.3	82533.6	785.8	374.7	40.8	100.0
PCS-B	0.0	996.4	3496.8	11692.4	82611.9	786.6	375.1	40.8	100.0
PCS-0.25	0.0	0.0	3532.0	11810.1	83443.3	794.5	378.8	41.2	100.0
PCS-0.5	0.0	0.0	0.0	12242.5	86498.5	823.6	392.7	42.8	100.0
PCS-1	0.0	0.0	0.0	0.0	98565.3	938.5	447.5	48.7	100.0
PSD-A	407.9	1317.9	4343.3	16538.6	71268.7	5652.6	442.9	28.1	100.0
PSD-B	0.0	1323.3	4361.1	16606.3	71560.6	5675.7	444.7	28.2	100.0
PSD-0.25	0.0	0.0	4419.6	16829.0	72520.3	5751.8	450.7	28.6	100.0
PSD-0.5	0.0	0.0	0.0	17607.2	75873.6	6017.8	471.5	30.0	100.0
PSD-1	0.0	0.0	0.0	0.0	92087.6	7303.8	572.3	36.4	100.0

*) The ratios between the different size fractions were determined after Williams screening and Endecotts sieving. The ratios for pine chip screenings containing all the fractions (PCS-A) were $f_A{:}f_B = 0.10$, $f_B{:}f_C = 0.28$, $f_C{:}f_D = 0.30$, $f_D{:}f_E = 0.14$, $f_E{:}f_F = 105.03$, $f_F{:}f_G = 2.10$ and $f_G{:}f_H = 9.18$. The ratios for pine sawdust containing all the fractions (PSD-A) were $f_A{:}f_B = 0.31$, $f_B{:}f_C = 0.30$, $f_C{:}f_D = 0.26$, $f_D{:}f_E = 0.23$, $f_E{:}f_F = 12.61$, $f_F{:}f_G = 12.76$ and $f_G{:}f_H = 15.74$. The total amount of wood was 100 g for all the studied furnishes and while removing the smallest size fractions, the ratios between the remaining size fractions were kept constant.

2.1.1 Impregnation conditions and procedures

The following conditions were applied during the impregnation experiments. The amount of wood was 100 g o.d. and the liquor-to-wood ratio was 8 l/kg. The EA charge was 17% NaOH on o.d. wood, and the impregnation liquor was prepared from industrial hot black liquor (HBL) (providing 10% NaOH on wood), industrial white liquor (WL) (providing 7% NaOH on wood) and distilled water. The initial EA concentration of the HBL varied between 31.1–32.9 g/l. The sulphidity of the WL was 38.2% and the EA concentration was 118.2 g/l.

The impregnation experiments were carried out in 1-litre autoclaves heated in a silicone oil bath. The wood material was placed in stainless steel baskets made of 200 mesh woven wire cloth located inside the autoclaves. The baskets were used for preventing wood material losses when the black liquor was drained off. The impregnation liquor was introduced and the autoclaves were pressurised with nitrogen to 1 000 kPa (= 10 bar) overpressure.

The impregnation temperature was 130 °C and the impregnation times were (0), 5, 10, 20, 40 and 60 min. The oil temperature was adjusted to a level, which exceeded the target by 2 °C to ensure that the temperature of impregnation liquor was correct.

The autoclaves were cooled in cold water for 5 min to stop the impregnation, and finally the black liquor was drained into a measure cylinder. The wood substance was thereafter centrifuged for 60 s by application of a centrifugal force of 100 g to separate the free liquor from the wood particles (SCAN-CM 43:95). The amount of this liquor was also recorded.

The impregnated wood material, which initially was 100 g, was put in a container, distilled water was added until a total weight of 2 000 g and it was leached for 48 h at room temperature. The leaching liquor was separated from the wood material and the wood material was subsequently washed with 2 000 ml of distilled water at room temperature, oven-dried at 105 °C and weighed for determination of its impregnation yield.

2.1.2 Analyses

The EA content of the white liquor was determined according to SCAN-N 30:85, but the EA content of the impregnation liquor, black liquor, drained black liquor and leach liquor was determined according to SCAN-N 33:94. Because the leaching liquor EA was relatively low, a known amount of sodium hydroxide was added to it to make sure that the accuracy of the titrator was sufficient enough for the alkali determination. The dry solids content of the impregnation liquor and drained black liquor was determined according to SCAN-N 1:61. Oxidation of the sodium sulphide increases slightly the black liquor weight, but the following reaction during drying was not taken into consideration.

$$2Na_2S + 2O_2 + H_2O \rightarrow Na_2S_2O_3 + 2NaOH$$
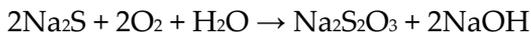
The following calculations were performed to obtain EA concentration leached from wood. The amount of EA of the impregnation liquor, $n_{EA,\ liquor}$ [mol], was calculated according to Equation 1.

$$n_{EA,\ liquor} = \frac{V_{in} \cdot c_0}{1000} \tag{1}$$

where V_{in} is the volume of the introduced impregnation liquor charged into the autoclave [ml] and c_0 is the initial EA concentration of the impregnation liquor [mol/l].

The density and dry solids of the drained black liquors were determined and examined for linear correlation which provided the equation as follows:

$$\rho = 0.002 \cdot X_{D.S.} + 1.035 \tag{2}$$

where ρ is the black liquor density [g/ml], and $X_{D.S.}$ is the black liquor dry solids [%]. The square of the correlation coefficient was 0.975.

The residual black liquor volume after the impregnation, V_{out} [l], was calculated by application of Equation 3.

$$V_{out} = \frac{V_{drained}}{1000} + \frac{m_{centrifuged}}{1000 \cdot \rho} \tag{3}$$

where $V_{drained}$ [ml] is the black liquor volume drained off from the autoclave, and $m_{centrifuged}$ [g] is the amount of black liquor subsequently removed by centrifugation from the wood material.

The residual alkali of the "black liquor" at 0 min was calculated according to Equation 4 and 800 ml was due to the liquor-to-wood ratio which was 8 l/kg.

$$c_{out,\ 0\ min} = c_0 \cdot \frac{V_{in}}{800} \tag{4}$$

The volume of the black liquor remaining in the wood after centrifugation, V_{wood} [l], was computed according to Equation 5.

$$V_{wood} = \frac{m_{wood,\,wet} - m_{wood,\,dry}}{1000 \cdot \rho} \tag{5}$$

where $m_{wood,\,wet}$ [g] is the amount wet wood obtained with centrifugation, and $m_{wood,\,dry}$ [g] the amount of oven-dry wood.

The leaching liquor alkali obtained from the impregnated and drained wood, $n_{EA,\,wood}$ [mol], was calculated by using Equation 6.

$$n_{EA,\,wood} = \frac{(2000 - m_{wood,\,dry}) \cdot c_{48\,h}}{1000} \tag{6}$$

where $c_{48\,h}$ is the alkali content of the final leaching liquor [mol/l], and 2 000 g is the total weight of the wood material and the leaching liquor.

Finally, the EA concentration leached from the wood, c_{wood} [mol/l], was calculated according to Equation 7.

$$c_{wood} = \frac{n_{EA,\,wood}}{V_{wood}} \tag{7}$$

Additionally, a repeatability test was performed using pine sawdust that contained all fractions. The wood material was impregnated for 30 min under the given conditions and the test was repeated 5 times.

2.2 Sawdust cooking [II]

2.2.1 Wood raw material

The air-dried wood raw material comprised hardwood and softwood sawdust and softwood chips. The softwood chips were screened with a Williams thickness screen to obtain 7–10 mm thick chips. Thick chips were used in order to obtain shives in pulp and clarify possible differences between the cooking techniques studied. The wood raw

material furnishes used in the experiments and prepared in the laboratory can be seen in Table 4.

Table 4. Wood raw material furnishes prepared in the laboratory. HW: hardwood, SW: softwood.

Wood	Furnish 1		Furnish 2	
	Share (%, w/w)	Weight (g o.d.)	Share (%, w/w)	Weight (g o.d.)
HW sawdust	4.0	32.0	3.2	25.6
SW sawdust	96.0	768.0	76.8	614.4
SW chips	-	-	20.0	160.0
Sum	100.0	800.0	100.0	800.0

2.2.2 Conventional sawdust cooking

In conventional sawdust cooking technique the cooking stage starts instantly when sawdust and hot cooking liquor are fed into the digester. Also, the entire amount of the cooking liquor is charged at the beginning of the cooking stage.

The cooking liquor containing HBL and WL was heated in a separate liquor heating vessel having a volume of 10 l. When the target temperature (180 °C) was achieved the actual digester was heated with steam for 10 min and subsequently filled with the wood raw material. The vessel containing the preheated liquor was pressurised to 12–13 bar with nitrogen gas and the liquor was fed into the digester. The digester was set to rotate and the electric heat mantle was switched on. The liquor was drained from the digester after the cooking stage and simultaneously cooled in a condenser for further analysis.

The digester was discharged and the pulp was washed on a 200-mesh screen with tap water until the wash filtrate was clear. The washed pulp was disintegrated for 10 min in a Wennberg disintegrator and pre-screened in a Valmet TAP03 screen with a slot size of 0.15 mm. The rejects were further screened in a Somerville screen with 0.15 mm slot size. The accept streams from both screens were collected and combined before centrifugation. The dewatered pulp was homogenised for 10 min and weighed. The reject was collected on a filter paper, dried in an oven and weighed.

The cooking conditions of the conventional sawdust cooking experiments can be seen in Table 5.

Table 5. Conventional sawdust cooking experiments.

Conventional cooking		1	2	3	4
Cooking	Chips (%, w/w)	20	20	20	-
	Sawdust (%, w/w)	80	80	80	100
	Temperature (°C)	180	180	180	180
	Time (min)	25	27	34	24
	EA charge (% NaOH on wood)	25	25	25	25

The liquor-to-wood ratio was 4.6 l/kg and the cooking liquor was prepared from industrial HBL (5% NaOH on wood), industrial WL (20% NaOH on wood) and distilled water. The industrial HBL was obtained from a Finnish pulp mill that produced softwood kraft pulp. The EA concentration of the HBL varied from 19.3 g/l to 20.6 g/l. The EA concentration of the WL was 107.3–108.8 g/l and sulphidity 39.2–40.3%.

2.2.3   Modified sawdust cooking

As mentioned in the previous chapter, in conventional sawdust cooking technique the entire amount of the cooking liquor is charged at the beginning of the cooking stage. Whereas, in the modified sawdust cooking technique, which contains an impregnation stage, the EA charge is divided between the impregnation and cooking stages.

The modified sawdust cooking technique started with the impregnation stage. The digester was first heated with steam and after 10 min filled with the wood raw material. Impregnation liquor was pumped into the digester through a heat exchanger. The electric mantle was switched on and the digester was set to rotate after a known amount of heated impregnation liquor (target temperature 130 °C), containing HBL and WL, was pumped into the digester.

In the cooking stage the cooking liquor containing only WL was also pumped into the digester through the heat exchanger unit. The unit was washed between the two stages. Also in the cooking stage, after a known amount of heated cooking liquor (target temperature 170 °C) was fed into the digester the digester was set to rotate. The

discharge of the digester and the pulp handling was conducted as in the conventional sawdust cooking procedure given in Chapter 2.2.2.

The cooking conditions of the modified sawdust cooking experiments can be seen in Table 6.

Table 6. Modified sawdust cooking experiments.

Modified cooking		1	2	3	4
Impreg-nation	Chips (%, w/w)	20	20	20	-
	Sawdust (%, w/w)	80	80	80	100
	Temperature (°C)	130	130	130	130
	Time (min)	25	25	25	25
	EA charge (% NaOH on wood)	17	17	17	17
Cook-ing	Temperature (°C)	170	170	170	170
	Time (min)	55	65	75	55
	EA charge (% NaOH on wood)	8	8	8	8

The liquor-to-wood ratio in the impregnation stage was 4 l/kg and the impregnation liquor was prepared from industrial HBL (5% NaOH on wood), industrial WL (12% NaOH on wood) and distilled water. After the impregnation pure industrial white liquor was charged into the digester (8% NaOH on wood) resulting in a slight increase of the liquor-to-wood ratio to 4.6 l/kg. The properties of HBL and WL are described in Chapter 2.2.2.

2.2.4 Bleaching and refining

The pulps obtained from the wood raw material furnish containing no chips, *i.e.* the experiment no 4 in Tables 5 and 6, were bleached using an elemental chlorine free ODE$_0$DE$_P$D bleaching sequence to a final brightness of approximately 87.6%. The bleaching experiments were performed at UPM-Kymmene Pulp Center in Pietarsaari, Finland. The bleached pulps were subsequently refined in a PFI mill (SCAN-C 24:96) using 0, 250, 500, 1 000 and 2 500 revolutions. Handsheets were then prepared and tested for physical properties.

2.3 Hydrotropic extraction [III]

2.3.1 Wood raw material

Industrial Nordic birch chips and Norway spruce chips and sawdust were used in the experiments. Nordic birch chips are a mixture of Silver birch (*Betula pendula*) and White birch (*Betula pubescens*). Wood chips were screened by a Williams chip thickness classifier. The slits of the applied screens were 6, 4 and 2 mm wide, and the employed screenings time was 10 min. The fractions retaining on the screen plates with 2 mm and 4 mm slits were regarded as accept chips. Bark, knots, rot and other impurities were removed by hand-picking from the accept chip fractions. While screening birch chips, the wood raw material which passed through the screen plate with 2 mm slits was collected and used as birch chip screenings.

2.3.2 Extraction conditions

Technical grade (assay ≥ 90%) sodium xylenesulphonate (SXS) mixture of isomers from Fluka was used in the extraction experiments. The extraction solvent was prepared by mixing 30 parts by weight SXS to 70 parts by weight distilled water.

The hydrotropic extraction conditions can be seen in Table 7. A 2.5-litre forced circulation reactor was used in the experiments excluding one experiment with birch chip screening where a 10-litre revolving reactor was used. The reactor was filled with wood and extraction solution. The temperature was increased from ambient temperature to targeted extraction temperature using a constant heating rate at 3 °C/min. The solution was drained from the reactor after the performed extraction and the spent extraction solution was stored for further analysis. The reactor was discharged and the extracted wood was first washed with 15% (w/w) SXS solution. Subsequently the wood was washed with hot water, disintegrated and centrifuged. After centrifuging, the extracted wood was again washed with hot water and centrifuged. Dry matter content and extraction yield of the wood was then determined.

Table 7. Hydrotropic extraction conditions. SC: spruce chips, SSD: spruce sawdust, BC: birch chips, BCS: birch chip screenings.

Wood Raw material	SXS (%, w/w)	Liquor to wood	Ramp (°C/min)	Temperature (°C)	Time at temperature (h)
SC	30	7.5:1	3	150	12
SSD	30	7.5:1	3	150	12
SSD*	-	7.5:1	3	150	12
BC	30	7.5:1	3	150	12
BCS	30	7.5:1	3	150	12

SSD*: only distilled water was used in the experiment.

2.3.3 Chemical analysis

The total lignin content of the wood samples was determined according to KCL method N:o 115b:82. The lignin content included the gravimetric lignin (insoluble in sulphuric acid) and the soluble lignin. Some of the lignin dissolves in the acid solution during the test and the acid-soluble lignin can be determined by a spectrophotometric method based on absorption of ultraviolet (UV) radiation at 203 nm.

The amount of hemicelluloses and pectins was determined by acid methanolysis-gas chromatography (GC) (Sundberg et al. 1996) with the following exceptions. The sample size was 10 mg with 0.01 mg accuracy. The sample was neutralised with 100 µl pyridine and 1 ml of internal standard solution containing 0.1 mg/ml sorbitol was added. 1 ml of fibre-free sample was evaporated under nitrogen gas flow and the dried sample was dissolved in 100 µl pyridine. The sample was silylated with a silylation solution containing 150 µl hexamethyldisilazane (HMDS) and 80 µl trimethylchlorosilane (TMCS) and analysed with GC the following day. The conversion factors applied to calculate the amounts of polysaccharides from the monosaccharide data were 0.90 for hexoses and 0.88 for pentoses.

2.3.4 Lignin isolation and characterisation

An aliquot of spent extraction liquor (1 ml) was taken from each experiment and mixed with 10 ml of distilled water or 10 ml of 0.1 M NaCl solution. The dilution ratio was thus 1:10. The mixture was centrifuged for 15 min and the liquid was decanted. The precipitate was then washed with 10 ml 0.1 M NaCl solution, centrifuged for 15 min and the liquid was decanted. This was repeated once more and the precipitate was thereafter freeze-dried and weighed, see Table 8.

Table 8. Precipitation process of lignin from the spent extraction solutions (all wood materials).

Spent extraction solution	Precipitation	1st washing	2nd washing
1 ml	10 ml 0.1 M NaCl 60 °C, 1 h	10 ml 0.1 M NaCl 60 °C, 1 h	10 ml 0.1 M NaCl 60 °C, 1 h
1 ml	10 ml distilled water 60 °C, 1 h	10 ml 0.1 M NaCl 60 °C, 1 h	10 ml 0.1 M NaCl 60 °C, 1 h
1 ml	10 ml 0.1 M NaCl 5 °C, 1 h	10 ml 0.1 M NaCl 5 °C, 1 h	10 ml 0.1 M NaCl 5 °C, 1 h
1 ml	10 ml distilled water 5 °C, 1 h	10 ml 0.1 M NaCl 5 °C, 1 h	10 ml 0.1 M NaCl 5 °C, 1 h

The carbohydrate content in the precipitates was analysed by acid methanolysis-GC (Sundberg et al. 1996), as described on page 24.

Fourier transform infrared (FT-IR) spectroscopy spectra of the precipitated and washed lignin samples were measured using a Perkin-Elmer Paragon 100 FT-IR apparatus. Approximately 1% to 3% by weight of the analysed sample was ground thoroughly with KBr and pressed into a pellet. A pure KBr pellet was used as a reference background. The scanning range varied from 2300–500 cm^{-1} and the resolution was 1 cm^{-1}.

2.4 Energy, kraft pulp and chemicals from wood chip screenings [IV]

2.4.1 Steam generation

The study focuses on a pulp mill that annually produces 500 000 tonnes of air-dry bleached softwood kraft pulp. Wood chip screenings are normally combusted with bark in a power boiler to generate heat and steam. The calculations of steam generation with chip screenings are presented in Tables 9 and 10 (Fogelholm and Suutela 2000). The following values are applied: wood density 400 kg/m^3, wood dry content 50%, lower (effective) heating value (LHV) of softwood material 19.2 MJ/kg, boiler efficiency 87%, high pressure (HP) steam pressure 8.4 MPa, temperature 480 °C and feedwater temperature 115 °C.

Table 9. Heat content in chip screenings according to Fogelhom and Suutela 2000.

Wood to cooking	5.1–5.5	m^3sub/ADt
Screening loss	1–3	%
Wood to screening	5.15–5.67	m^3sub/ADt
Chip screenings	0.052–0.170	m^3sub/ADt
Wood density	400	kg/m^3s
Wood dry solids	50	%
Wood to firing	41.2–136.1	kg/ADt
LHV in dry solids	19.2	MJ/kg
LHV as fired	8.38	MJ/kg
Wood heat content	0.35–1.14	GJ/ADt

Table 10. Steam generation from chip screenings according to Fogelholm and Suutela 2000.

Chip screenings fired	0.35–1.14	GJ/ADt
Boiler efficiency	87	%
Heat to steam	0.30–0.99	GJ/ADt
HP steam pressure	8.4	MPa
Temperature	480	°C
Specific enthalpy	3.345	GJ/t
Feedwater temperature	115	°C
Specific enthalpy	0.485	GJ/t
Steam generation	0.11–0.35	t/ADt

According to Tables 9 and 10 the heat content of chip screenings varies between 0.35–1.14 GJ/ADt and depends on the wood consumption and the extent of screening loss. When HP steam is generated according to Table 10 the amount of steam is 0.11–0.35 t/ADt.

2.4.2 Kraft pulping

Chip screenings can also be used in kraft pulp production. The particle size distribution of chip screenings and sawdust from the same softwood species is very similar. Additionally, the fibre dimensions are close to each other (Korpinen and Fardim 2006). For bleachable grade sawdust pulp the yield is 43–45% and for unbleached sawdust pulp the yield is 46–48% (Bail 1979). The yield difference for sawdust is 2.1–2.7% less than from chips of the same

wood species (Bail 1979; Arends and Donkersloot-Shouq 1985). The bleaching yield of sawdust pulp is about 90% (Isotalo et al. 1964a) therefore the yield of bleached sawdust pulp is ranging from 38.7–40.5%.

2.4.3   Production of ethanol

Theoretically, approximately 410 litres ethanol can be produced per o.d. tonne wood raw material using only the hexose fraction and 455 litres using all carbohydrates (Galbe and Zacchi 2002). The theoretical value of 455 l was used in the calculations when estimating the amount of ethanol that can be produced from wood chip screenings.

2.4.4   Production of high added value chemicals

There are other various products than ethanol that can be produced from biomass using different conversion processes, as seen in Figure 9 (Kamm and Kamm 2004; Taherzadeh and Keikhosro 2007).
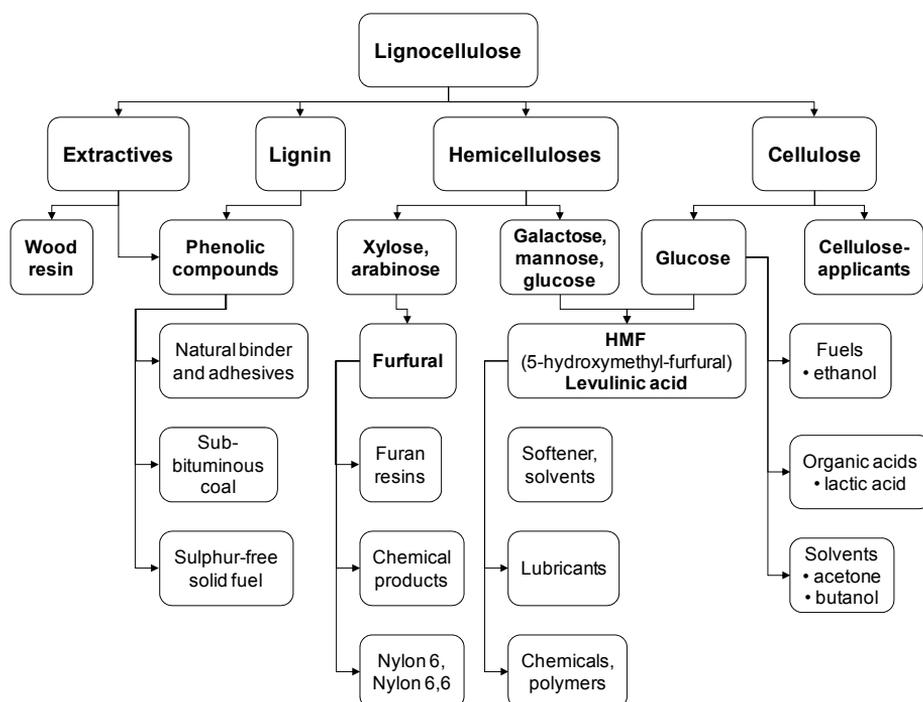
Figure 9. Composition of lignocellulosic materials and converted products, redrawn from Kamm and Kamm 2004; Taherzadeh and Keikhosro 2007.

The United States Department of Energy has published a list of the top 12 bio-based chemicals (Werpy et al. 2004). The list was shortened from over 300 chemicals and the selection criteria were biomass precursors (carbohydrates, lignin, fats and proteins), process platforms, building blocks, secondary chemicals, intermediates, products and final applications. The selected chemicals are presented in Table 11.

Table 11. Top 12 bio-based chemicals from all sources of biomass components (Werpy et al. 2004).

Carbon number	Chemical
4	1,4 succinic, fumaric and malic acids
6	2,5-furan dicarboxylic acid
3	3-hydroxy propionic acid
4	aspartic acid
6	glucaric acid
5	glutamic acid
5	itaconic acid
5	levulinic acid
4	3-hydroxybutyrolactone
3	glycerol
6	sorbitol
5	xylitol/arabinitol

2.4.5 Wood materials

Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) wood chip screenings were collected from a Finnish pulp mill. The spruce/pine chip screenings were obtained from a wood furnish containing 50% of spruce chips produced on site and 50% of pine sawmill chips. The pine chip screenings were obtained from a wood furnish containing 80% of pine chips produced on site and 20% of pine sawmill chips.

The extractive content of the samples were determined by using a Dionex Corp. Accelerated Solvent Extraction (ASE) apparatus. The lipophilic extractives were first extracted with hexane. The hydrophilic extractives were then extracted with a mixture of acetone and water (95:5 v/v) (Ekman and Holmbom 1989; Örså and Holmbom 1994; Willför et al. 2003).

The total lignin content was determined for the extractive free wood samples according to KCL method N:o 115b:82.

The carbohydrate content was determined for the extractive free wood samples. The amount of hemicelluloses was determined by acid methanolysis and the amount of cellulose was determined by acid hydrolysis (Sundberg et al. 1996) with the following exceptions. In acid hydrolysis, the sample size was 10 mg with 0.01 mg accuracy and 0.2 ml of 72% sulphuric acid was added and the sample was kept at room temperature for 2 hours. 0.5 ml of deionised water was added and the sample was kept at an ambient temperature for 4 hours after which 6.0 ml deionised water was added. The secondary hydrolysis was performed the following day by autoclaving at 125 °C for 90 min. 1 ml of internal standard containing 5 mg/ml sorbitol was added. 1 ml of hydrolysate was evaporated under nitrogen gas flow and silylated with a silylation solution containing 80 μl pyridine, 170 μl HMDS and 70 μl TMCS. The silylated sample was analysed with GC the next day. Acid methanolysis is described in Chapter 2.3.3.

The conversion factors applied to calculate the amounts of polysaccharides from the monosaccharide data were 0.90 for hexoses and 0.88 for pentoses.

2.5 Sawdust reinforcement fibre (RIF) pulp [V]

Unbleached sawdust kraft pulp was collected at a Finnish pulp mill from the thickener after pulp washing and screening, *i.e.* pulp that goes to the paper machine. Peroxide bleached Norway spruce thermomechanical pulp (TMP) and pressurised groundwood pulp (PGW) were collected at a Finnish paper mill. Unbleached sawdust pulp was bleached using a D_0-E_P-D_1-E_P sequence to an ISO-brightness of 83.5%. Bleached sawdust pulp was refined with Valley beater according to ISO 5264-1 to °SR 33 and the drainability of pulp samples was determined using Schopper-Riegler method according to ISO 5267-1. Approximately 60 g/m² handsheets were made according to SCAN-C 26:76. No draining time was applied after the sheet was formed on the wire screen. Sheets containing mechanical pulps were made with a white water circulation. The pressing was done according to ISO 5269-1 and the handsheets were conditioned according to ISO 187. Apparent density was determined according to ISO 534, tensile strength according to ISO 1924-2 and tear strength according to ISO 1974. Brightness, opacity and light-scattering

coefficient were determined according to ISO 2470 and ISO 2471. Air resistance was determined according to ISO 5270. The pulp samples were also analysed with a Kajaani FiberLab Analyzer. The measuring speed was approximately 90 fibres per second and the analysis consistency of the sample was 0.015–0.025% for pulps with longer fibres (TMP) and 0.005–0.01% for pulps with shorter fibres (PGW and sawdust pulps) (Mörseburg et al. 1999).

Unrefined and refined bleached sawdust pulp was blended with TMP and PGW pulps according to Table 12.

Table 12. Blends of different pulp furnishes (%, w/w). The freeness of refined sawdust pulp was 33 °SR.

Sawdust pulp, unrefined/refined	TMP	PGW
0	100	100
5	95	95
15	85	85
30	70	70
45	55	55
100	0	0

The production costs of bleached softwood kraft pulp, bleached mechanical pulp and bleached sawdust kraft pulp are estimated using the price of wood because it is the greatest cost factor. The wood consumption for producing different bleached pulps can be calculated according to Varhimo et al. 2003.

$$W_{cons} = \frac{0.9}{(1-b) \cdot \rho \cdot Y}$$

where W_{cons} = wood consumption, solid m^3/admt (solid cubic metre per air-dry metric tonne of pulp)
b = bark content, fractional
ρ = o.d. wood density, t/m^3
Y = yield of o.d. bleach pulp, fractional

The following data are applied when calculating the wood consumption of the different pulps. The bark content of Norway spruce wood is 9.3% (Björklund 2004). The wood density is 400 kg/m^3

and dry content 50% (Duchesne et al. 1997). The yield of bleached reinforcement kraft pulp is 45.5% (Kovasin and Tikka 1993), the yield of bleached TMP is about 92% (Holmbom et al. 2005) and the yield of bleached sawdust kraft pulp is ca 39.5% [Paper IV]. The bark content in sawdust is ignored because it cannot be removed before the kraft pulping. The wood consumption is hence 5.45 solid m^3/admt for bleached RIF, 2.70 solid m^3/admt for bleached mechanical pulp and 5.70 solid m^3/admt for bleached sawdust kraft pulp. Sawdust is usually delivered as bulk product to the pulp mills. One loose m^3 equals to about 300 kg in typical moisture content (Alakangas 2005), hence the amount of sawdust needed for 5.92 solid m^3/admt wood consumption is 15.2 loose m^3/admt.

3 Results and discussion

3.1 Black liquor impregnation [I]

The repeatability test using the pine sawdust containing all the fractions was performed and a relative standard deviation was obtained by multiplying the standard deviation by 100% and dividing this product by the mean.

The relative standard deviation for EA concentration in black liquor, EA concentration released from the impregnated wood and wood yield after impregnation was 2.21%, 4.50% and 0.87%, respectively [Paper I].

3.1.1 EA concentration in drained black liquor

The EA concentration of the drained black liquors decreased with increased impregnation time, as seen in Figure 10. The legends in the following figures are defined in Tables 13 and 14. Additional information can be seen in Table 3 (p. 18).

Table 13. Pine chip screenings fractions used in the experiments.

	Bark	<0.25	<0.50	<1.00	>1.00	mm
PCS-A	+	+	+	+	+	
PCS-B		+	+	+	+	
PCS-0.25			+	+	+	
PCS-0.5				+	+	
PCS-1					+	

PC: pine chips

Table 14. Pine sawdust fractions used in the experiments.

	Bark	<0.25	<0.50	<1.00	>1.00	mm
PSD-A	+	+	+	+	+	
PSD-B		+	+	+	+	
PSD-0.25			+	+	+	
PSD-0.5				+	+	
PSD-1					+	

PC: pine chips

EA in black liquor (mol/l)

Impregnation time (min)

EA in black liquor (mol/l)

Impregnation time (min)
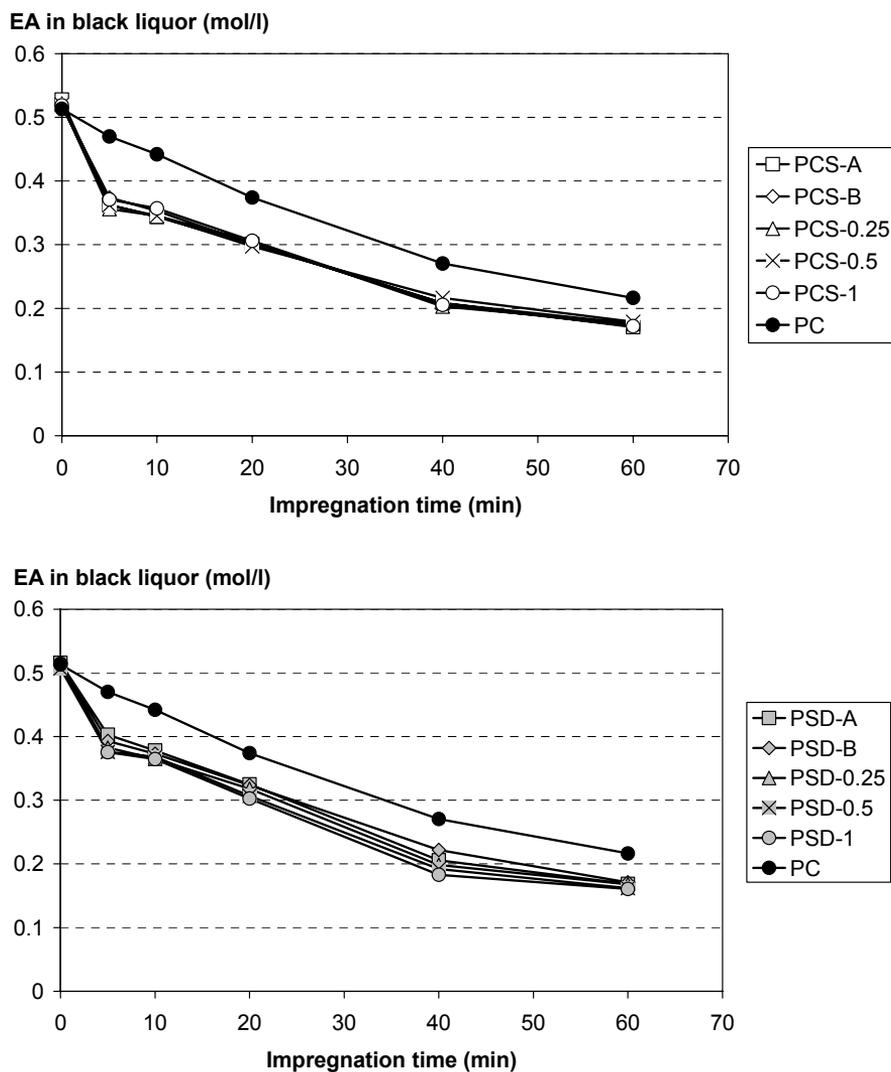
Figure 10. Effective alkali (EA) of the black liquor drained from the impregnation of pine chip screenings (PCS, upper), pine sawdust (PSD, lower) and pine chips (PC, upper and lower) as a function of time.

The EA concentration of the black liquor after the impregnation of pine chips was higher than that of chip screenings and sawdust during the entire impregnation. This implies that pine chips consumed less EA than the finely divided wood materials. This is probably due to the different surface area between chips and finely divided wood material. The surface area of pine chips is much smaller

than the surface area of chips screenings and sawdust preventing active ions in the impregnation liquor from penetrating and diffusing into the wood.

The initial decrease of the EA was fast in the chip screenings and the sawdust, and for both of these wood materials the EA concentration was lower than that obtained with regular pine chips. For the first 10 min of impregnation the black liquor EA appeared to be lower for the chip screenings than for the sawdust impregnation, but practically this difference disappeared after 20 min. A removal of the smallest fractions was seen to slightly affect the results obtained with various sawdust furnishes, but not clearly seen with the wood chip screenings. The reason is probably due to differences in morphology and accessibility.

3.1.2   EA concentration released from the impregnated wood

After the impregnation experiment the liquor was drained from the autoclave and the free liquor was removed from surface of the wood particles by centrifuging. The impregnated wood material which contained a remaining quantity of impregnation liquor was then leached in distilled water for a period of time, see Chapter 2.1.1. The amount of residual EA (mol) of the leaching liquor was determined and the EA concentration (mol/l) which was released from the impregnated wood was calculated on the basis of volume impregnation liquor absorbed by the impregnated wood material after draining and centrifuging.

The various wood materials absorbed a large amount of liquor and consequently the EA concentration of the wood materials increased rapidly, particularly because they were air-dried, see Figure 11.

EA in wood (mol/l)

Impregnation time (min)

EA in wood (mol/l)

Impregnation time (min)
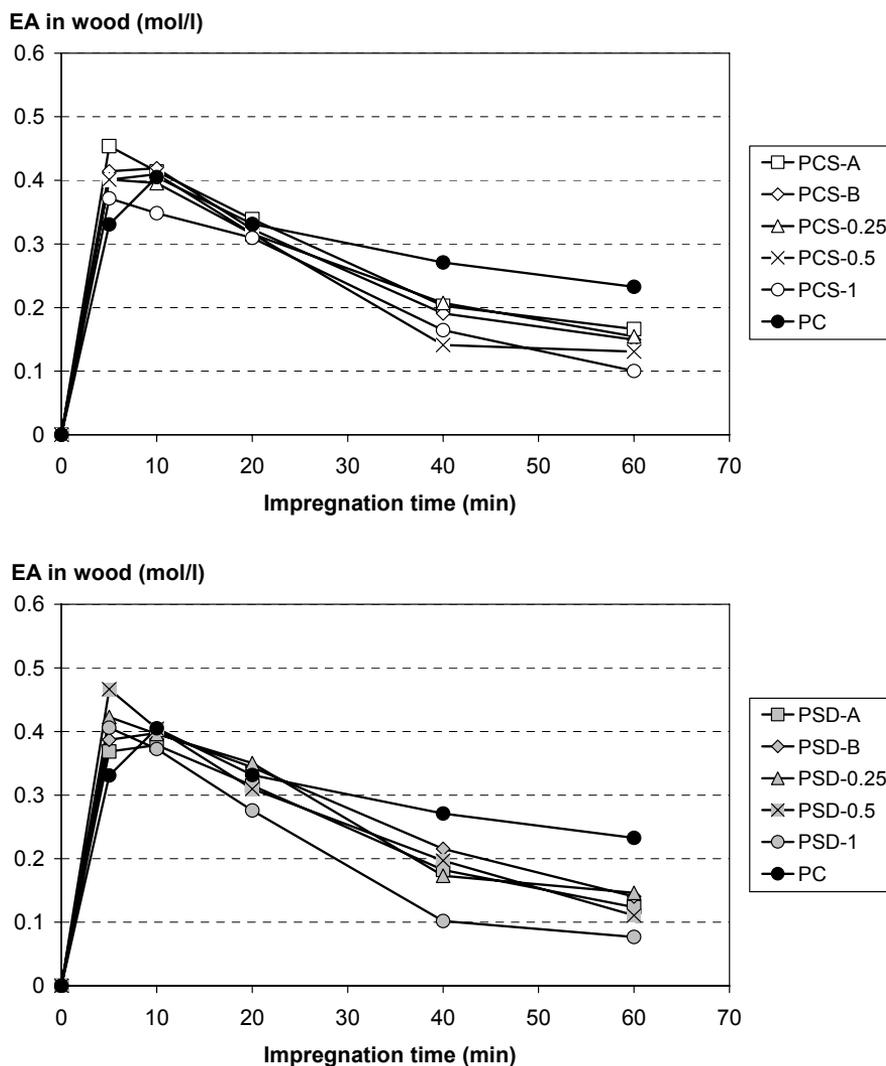
Figure 11. Effective alkali (EA) released from wood during impregnation in pine chip screenings (PCS, upper), pine sawdust (PSD, lower) and pine chips (PC, upper and lower) as a function of time.

The EA concentration built up in the chip screenings and the sawdust during the impregnation exceeded initially the concentration of the surrounding liquor as shown in Figures 10 and 11, which normally would not be expected. Similar results have been obtained in a study performed with refiner mechanical pulp (RMP) (Hultholm 2004). The difference in concentration may be theoretically explained by a

Donnan equilibrium, which is characterised by an uneven distribution of diffusing ions between two ionic solutions—of which one or both may be gelled—that are separated by a membrane impermeable to at least one of the ionic species being too large to penetrate the membrane pores. The same action as a membrane may be provided by other restraints, *e.g.*, a gel and a field of gravity, which might prevent some ionic components, but not all, from moving from one phase to another (Gold et al. 1987). It is suggested that the EA concentration in fine wood particles and chips are not directly comparable, since the leaching may affect them in a different way. Different amounts of organic compounds with acid-base properties may be extracted and thus the dissimilar acid consumption during titration would subsequently provide different EA concentrations. In addition, the titration method itself may affect the results. It has been observed that the SCAN titration method gives a higher EA concentration than the so-called Wilson titration method (Wilson 1968; Korpinen 2002). The difference may even be strengthened by the extremely low HO^- concentration of the leaching liquor. The EA concentration inside the sawdust and the chip screenings started to decrease beyond 10 min of impregnation due to the alkali consuming reactions and dropped below the concentration of the surrounding liquor. Furnishes containing most of the fractions seemed to provide the highest level of EA. The time required to achieve the same average EA concentration inside the chip screenings and the sawdust as in the surrounding liquor was calculated from the obtained titration data and it was commonly 20 min, as accordingly it was 40 min for the chips.

3.1.3 Wood yield after impregnation

Figure 12 confirms that the yield of the raw material decreased during the impregnation process. As expected, the yield obtained with the chip screenings and the sawdust was lower than that of the regular chips, because they absorbed more impregnation liquor and also consumed more EA than the chips.
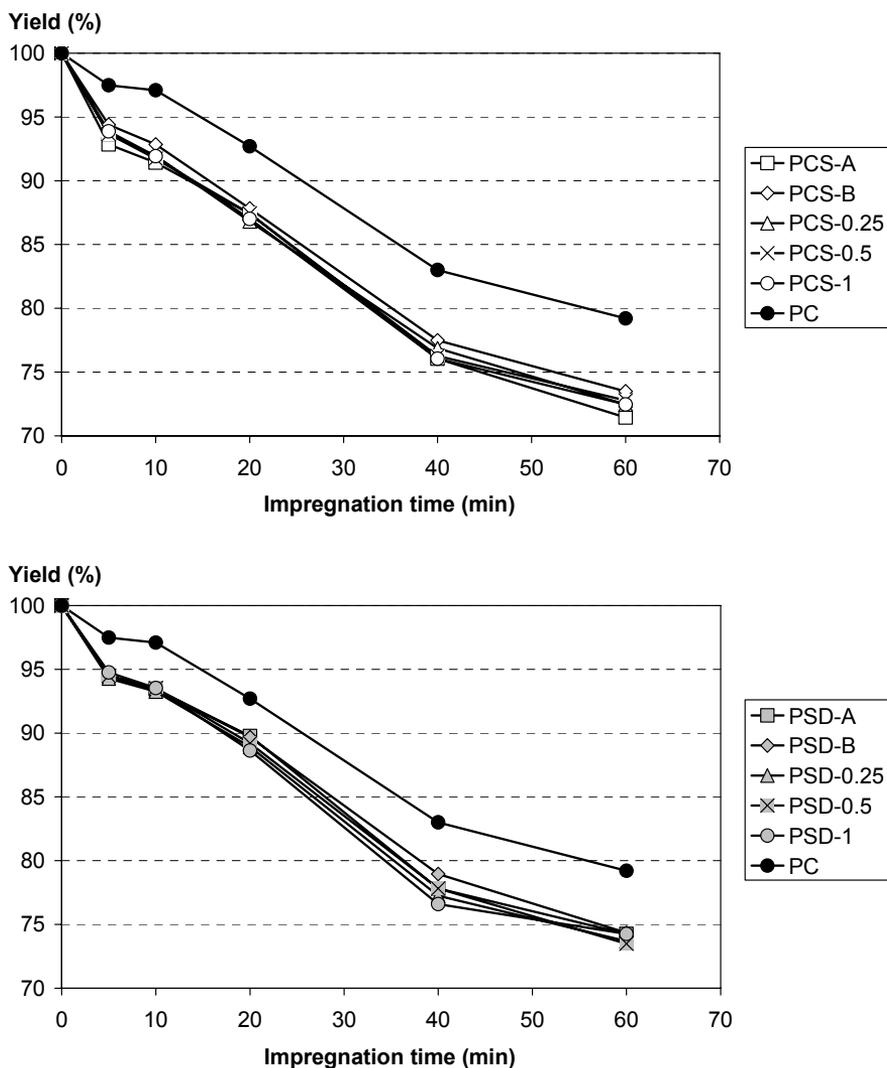
Yield (%)

Yield (%)

Figure 12. Wood yield after impregnation of pine chip screenings (PCS, upper), pine sawdust (PSD, lower) and pine chips (PC, upper and lower) as a function of time.

Approximately 15–25% of the lignin and 40% of the hemicelluloses are dissolved in the initial phase of a conventional softwood kraft cooking. Accordingly about 50% of the EA is consumed in neutralisation of acidic reaction products formed when extractives and carbohydrates are dissolved or cleaved (Rekunen et al. 1980; Alén 2000). The impregnation yield differences between chips and sawdust

could be the reason that the yield after cooking is higher for regular chips than for fine wood particles. The pine chip screenings provided a lower yield than the sawdust during the entire impregnation, possibly because the initial material contained more bark. Also the chemical composition of the wood materials was different, *i.e.* the chip screenings contained slightly less carbohydrates and much more extractives (Korpinen and Fardim 2006). Bark particles are smaller than wood particles produced in the same wood handling operations. Therefore they tend to disperse into the black liquor during continuous cooking. Additionally, bark consumes more cooking chemicals and increases the dry solids content and subsequently the total organic carbon (TOC) content of the black liquor (Bail 1979).

3.2 Sawdust cooking [II]

3.2.1   Cooking results with 20% chips addition

The modified cooking method, described in Chapter 2.2.3, resulted in lower kappa number than the conventional cooking method (Chapter 2.2.2) at a given H-factor, as seen in Figure 13.
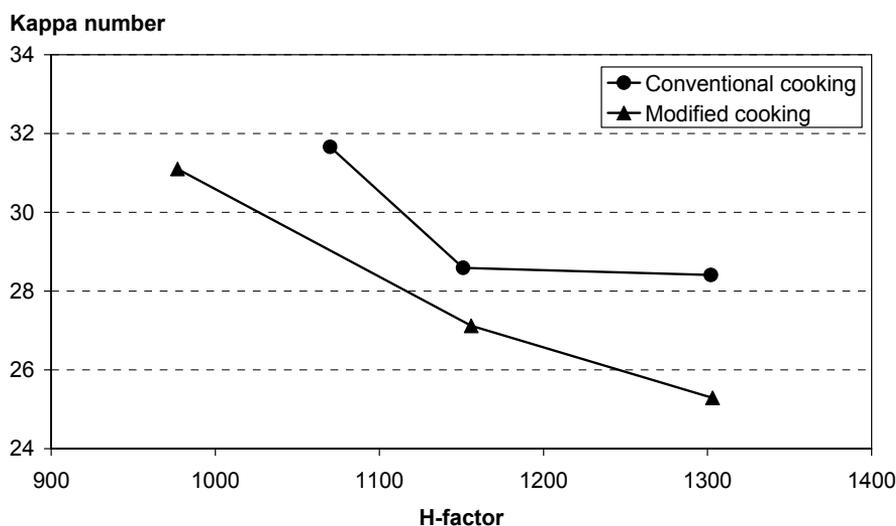
Figure 13. Kappa number as a function of H-factor.

The duration of the modified cooking method was longer compared to the conventional cooking method due to the impregnation stage

and the lower cooking temperature applied. Nevertheless, the impregnation stage at 130 °C contributes slightly to the H-factor, only 10.5 units. Kappa number indicates the residual lignin content of pulp. Thus, the pulp produced with the modified cooking method contained less lignin than the pulp that was produced with conventional cooking.

The total yield of the conventional cooking method was higher than that of the modified cooking, see Figure 14.
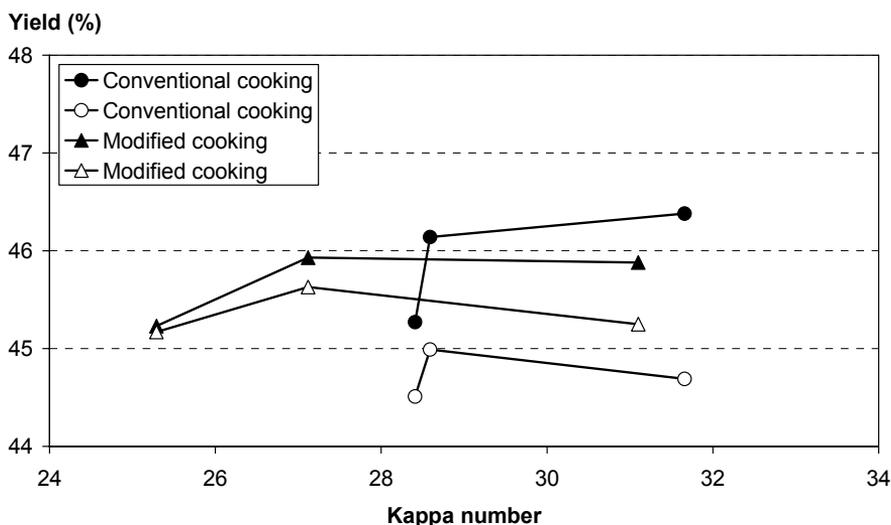
Figure 14. Total (solid symbol) and screened yield (hollow symbol) as a function of kappa number.

Because of the considerably higher shives content, the screened yield of the conventional cooking was lower. The high shives content was due to the lack of the impregnation stage. The fast heating time led to a delignification that apparently occurred only on the surface of the wood particles. Hence, the alkali concentration inside the wood decreased and resulted in incomplete disintegration.

3.2.2   Bleaching and refining

A wood raw material furnish without any chips addition (Table 4) was cooked using both of the cooking methods. The kappa numbers of the pulps obtained by the conventional and modified cooking methods were 27.7 and 26.4, respectively.

In the beginning of the bleaching the kappa number of the pulp produced by the conventional cooking method was slightly higher than the kappa number of the pulp produced by the modified cooking method. Although, the difference in the kappa number disappeared in the final D-stage, as is shown in Figure 15.
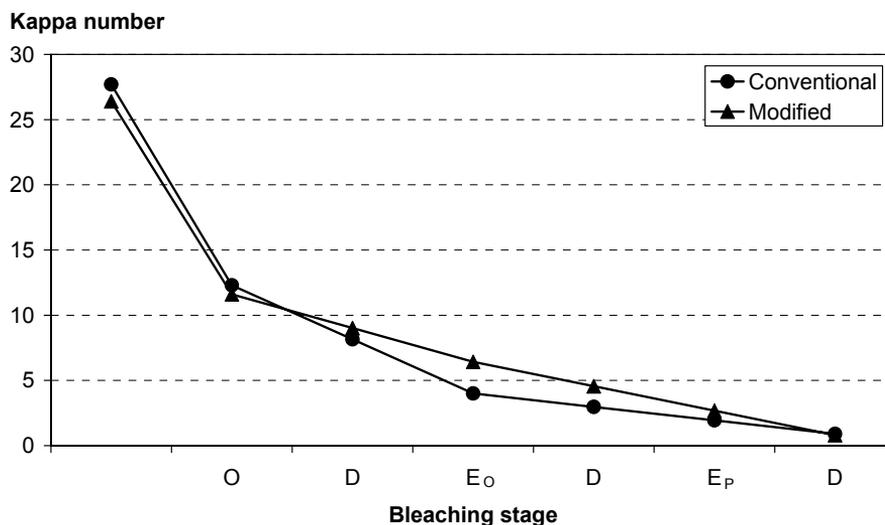
Figure 15. Kappa number as a function of the bleaching stage.

During bleaching to approximately 87.7% ISO-brightness the pulp produced by the conventional cooking method consumed 38.2 kg/ADt ClO_2. On the other hand, the pulp produced with the modified cooking method consumed 36.6 kg/ADt. Consequently, the chlorine dioxide consumption decreased slightly when the modified cooking method was applied prior to bleaching.

The intrinsic viscosities of the pulps were determined according to SCAN-CM 15:88 using copper ethylenediamine (CED) solution and it can be seen in Figure 16 that the viscosity of the pulps decreased during the bleaching.
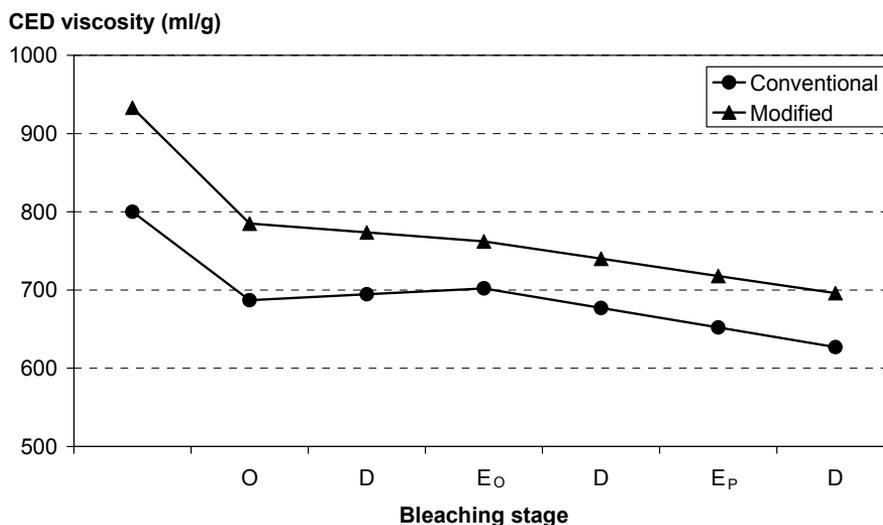
Figure 16. Intrinsic viscosity as a function of the bleaching stage.

The viscosity of the pulp produced by the modified cooking method was higher prior to the bleaching, although it had a slightly lower kappa number. The viscosity difference remained constant through the bleaching sequence. According to Figure 16 the degradation of cellulose chains was not so extensive when the modified cooking method was used for the production of sawdust kraft pulp.

The fully bleached pulps were refined by application of a PFI-beater. Laboratory handsheets were prepared and tested after 0, 250, 500, 1 000 and 2 500 revolutions and some of the most important results are presented in Figures 17, 18, 19 and 20.

The °SR number, *i.e.* the drainage resistance increased with increased revolutions. The initial level of the °SR number was higher for the pulp that was produced by the conventional cooking method and the difference between the pulps remained unchanged in the beginning of the refining, as shown in Figure 17.

°SR
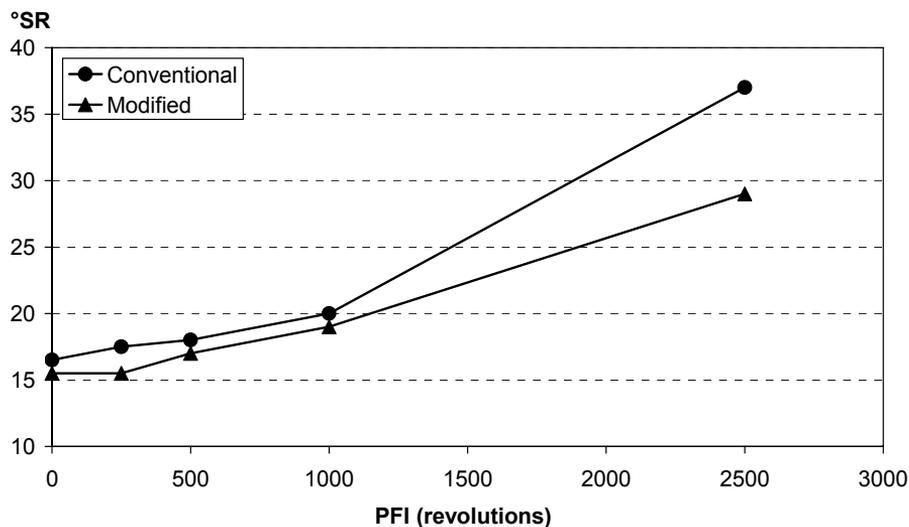
Figure 17. Schopper-Riegler number as a function of PFI revolutions.

This implies that both of the pulps were refined equivalently in the initial stages of refining. The difference in °SR number became greater after the fourth refining point, where the pulp produced by the modified cooking method drained more easily, probably due to the less damaged cellulose chains which were resistant to refining. It is also possible that the pulp produced by the conventional cooking method generated more fines during refining, thus increasing the drainage resistance.

As shown in Figure 18, the tear index decreased with increased tensile index. As expected, no major differences were found between the pulps.

Tear index (mNm^2/g)
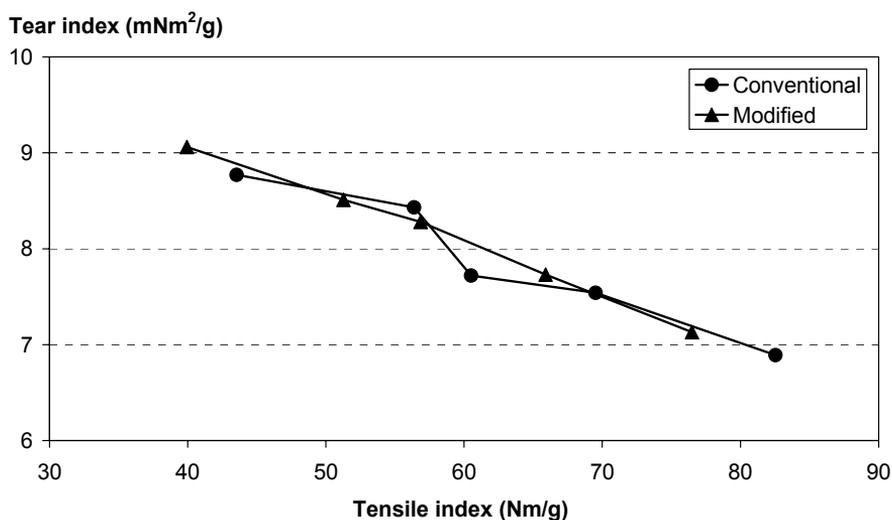
Figure 18. Tear index as a function of tensile index.

The tear index was low because of the short fibres in the pulps. Since no differences existed between the strength values, the tensile and tear indices were also evaluated as a function of the sheet density and zero-span tensile strength. The strength properties as a function of the sheet density relate to the level of bonding. Increased bonding contributes to higher sheet strength, decreased linting tendency and a better sheet consolidation (Cannel 1999).

The tear index decreased with the increasing sheet density, as shown in Figure 19.
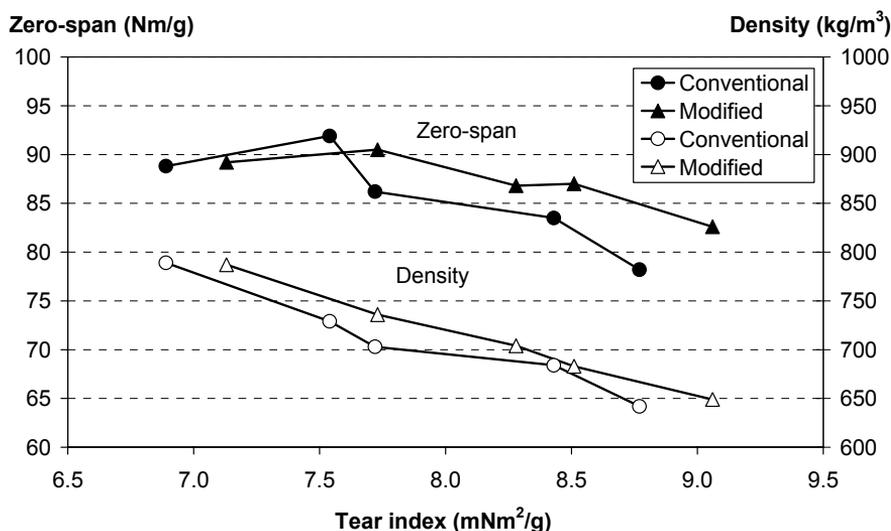
Figure 19. Zero-span tensile strength (solid symbol) and apparent sheet density (hollow symbol) as a function of the tear index.

Higher tear strength of the pulp produced by the modified cooking method is probably due to a lower degree of refining, higher fibre strength and lower degree of bonding. On the other hand, lower tear strength of the pulp produced by the conventional cooking method is likely to be caused by fibres with low strength in combination with higher degree of bonding.

The tensile index increased when the sheet density was increasing, as illustrated in Figure 20, and the tensile strength of the pulp produced by the conventional method was slightly higher at a given sheet density.
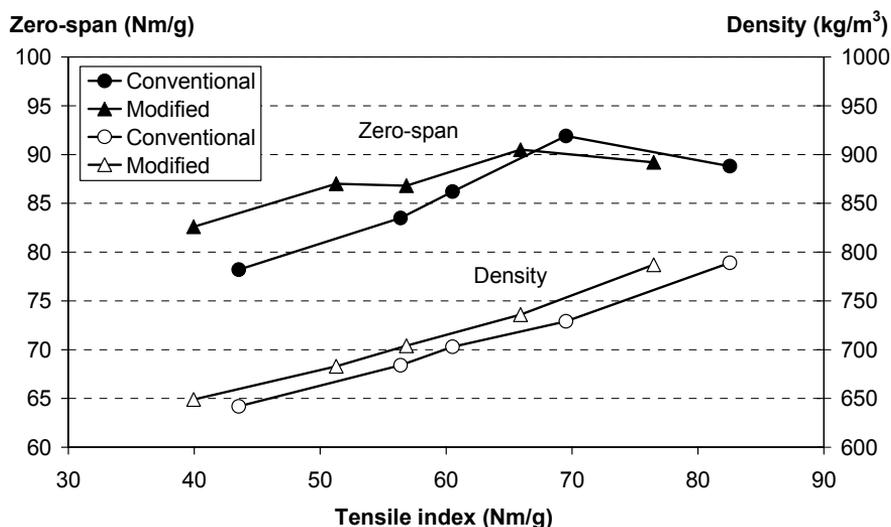
Figure 20. Zero-span tensile strength (solid symbol) and apparent sheet density (hollow symbol) as a function of the tensile index.

The higher tensile strength at a given sheet density of pulp produced by the conventional cooking method is probably due to more collapsed fibres and hence higher degree of bonding. In addition, increased fines content of the pulp contributes to tensile strength which can also explain the higher drainage resistance and higher air resistance.

3.3 Hydrotropic extraction [III]

3.3.1 Extraction of lignin

After SXS extraction up to 70.1% of lignin was extracted from Nordic birch, see Table 15. Unexpectedly, the extraction of lignin was not as efficient with Nordic birch chip screenings as with Nordic birch chips. Industrial Nordic birch chip screenings had been fractionated and the bark content of the different size fractions was determined (Korpinen and Fardim 2006). It was found that the birch chip screenings were contaminated with bark. The bark content was high in the smallest size fractions and increased substantially with decreasing particle size, from 10% up to 56%. This may explain the lower lignin extraction yield because there are more guaiacyl units in birch bark compared to

the birch wood (von Andersson et al. 1973). In addition, birch bark contains more lignin matter than birch wood (Jensen 1948; Kuznetsova et al. 2005).

Table 15. Wood yield after extraction and lignin extraction yield of the different raw materials (%).

Wood raw material	Wood yield after extraction	Lignin extraction yield
Norway spruce chips	68.8	20.0 ± 1.2
Norway spruce sawdust	51.9	38.3 ± 1.7
Norway spruce sawdust*	76.2	5.5 ± 2.4
Nordic birch chips	54.4	70.1 ± 7.2
Nordic birch chip screenings	62.3	46.9 ± 5.9

SSD: only distilled water used in the experiment.*

The lignin structure of hardwood (Sy/Gu) may explain the difference in the extraction of lignin between Norway spruce and Nordic birch chips. There are qualitative and quantitative differences in lignin distribution. Softwoods have highly lignified middle lamella containing mainly guaiacyl lignin and less lignified secondary wall containing guaiacyl lignin. The distribution of lignin in secondary wall and middle lamella of hardwood fibres is similar to that in softwood fibres but the secondary wall is less lignified and it contains a mixture of guaiacyl and syringyl lignin (Donaldson 2001). Hardwood lignin contains a higher methoxyl content, is less condensed and is more prone to chemical conversion than softwood lignin (Ramos 2003). For example in a previous study, acidolysis of birch wood has yielded more phenolic monomers than spruce wood (Lundquist and Lundgren 1972). In another study (Yasuda et al. 2001), it was found that acid-soluble lignin content was higher with syringyl lignin rich wood than with guaiacyl lignin rich wood.

The extraction of lignin was more efficient with Norway spruce sawdust than with Norway spruce chips. Both Norway spruce chips and sawdust contain mainly guaiacyl lignin and therefore the lignin structure cannot solely explain the difference in the degree of lignin extraction. It is believed that hydrotropic SXS molecules adsorb on the cell wall and disorganise its structure. Thereafter SXS and water molecules penetrate the cell wall and access the lignin and solubilise it (Raman and Gaikar 2002). Therefore the capillary structure of wood plays an important role. Although hardwood is denser than softwood,

it is easier to penetrate because it contains vessel elements which have a large diameter. The penetration in hardwood is very small across the grain because its pit membranes are not very porous, which retards the introduction of liquor into neighbouring cells (Stone and Förderreuther 1956; Clayton et al. 1989). Softwoods do not contain vessel elements, and hence the penetration occurs mainly from lumen to lumen via the porous pits. Also the resin canals and rays conduct liquids in softwood (Matsumara et al. 1999). Penetration in softwood latewood is easier than in softwood earlywood which is due to pit aspiration. However, hardwoods show small difference in penetration between latewood and earlywood because the pits cannot be aspirated (Siau 1995). Pit aspiration usually occurs when sapwood is transformed into heartwood or when wood dries. In softwoods, the torus seals one of the pit apertures and, therefore, blocks the passage through the pit (Usta 2005). The pit aspiration in Norway spruce sawdust does not have significant effect on penetration. The sawdust particles are small and therefore it contains more broken fibres and surfaces where the extraction solution can penetrate the wood matrix.

To sum up, it can be stated that the type of lignin (hardwood lignin vs. softwood lignin), the particle size of wood (accessibility) and the bark content of wood have a significant impact on the hydrotropic extraction of lignin.

3.3.2   Lignin isolation and characterisation

Lignin precipitation experiments were carried out to all spent extraction solutions using one part of spent hydrotropic extraction solution and ten parts of distilled water or 0.1 M NaCl solution, as described in Chapter 2.3.4. The amount of precipitated lignin was determined after freeze-drying and weighing and it was found to vary from 6.9 g/l (Norway spruce chips) to 24.3 g/l (Nordic birch chips), as illustrated in Figure 21.

Lignin precipitation (g/l)
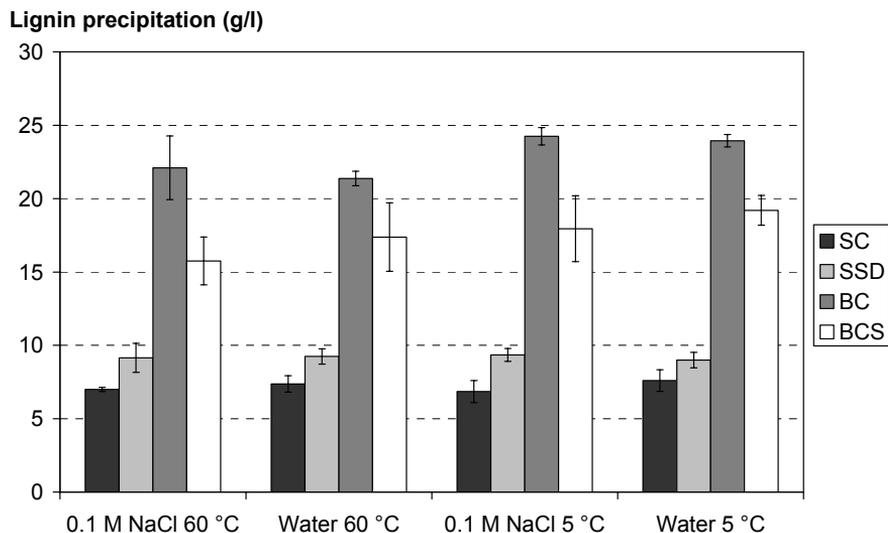
Figure 21. Lignin precipitation from spent hydrotropic extraction solution. SC: spruce chips, SSD: spruce chip screenings, BC: birch chips, BCS: birch chip screenings.

The amount of precipitated lignin correlated well with the amount of extracted lignin, see Table 15. The square of the linear correlation coefficient between the hydrotropic extraction yield of lignin and the amount of precipitated lignin was 0.965.

The carbohydrate content in different precipitated lignin samples was determined by acid methanolysis-GC to determine the possibly remaining lignin carbohydrate complexes in the precipitates. It can be seen in Table 16 that the different precipitated lignin samples contained very small amounts of carbohydrates, less than 10 mg/g or 0.1% w/w. Therefore it can be concluded that only small amounts of lignin carbohydrate complexes may be remained in the precipitates.

Table 16. Carbohydrate composition of the precipitated lignin samples (mg/g).

	Ara	Rha	Xyl	GlcA	GalA	4-O-Me-GlcA	Man	Gal	Glc	Tot
Spruce chips										
0.1 M NaCl 60 °C	1.0	0.0	0.6	0.2	0.4	0.0	3.5	1.0	1.3	8.2
Water 60 °C	0.7	0.0	0.5	0.2	0.5	0.0	3.2	1.1	1.2	7.4
0.1 M NaCl 5 °C	0.3	0.2	0.5	0.4	0.4	0.0	2.4	0.8	0.9	5.8
Water 5 °C	0.6	0.0	0.5	0.4	0.6	0.0	3.4	1.1	1.6	8.2
Spruce sawdust										
0.1 M NaCl 60 °C	0.8	0.0	0.4	0.1	0.1	0.0	2.3	0.8	0.8	5.2
Water 60 °C	1.3	0.1	0.4	0.2	0.3	0.0	2.3	0.7	0.8	6.1
0.1 M NaCl 5 °C	1.4	0.1	0.6	0.3	0.8	0.0	3.0	1.0	1.1	8.3
Water 5 °C	1.4	0.1	0.4	0.3	1.0	0.0	2.8	1.0	1.0	8.0
Birch chips										
0.1 M NaCl 60 °C	0.6	0.1	1.2	0.1	0.8	0.0	0.8	0.9	0.4	4.9
Water 60 °C	0.6	0.1	1.6	0.1	0.9	0.0	0.6	0.7	0.4	4.9
0.1 M NaCl 5 °C	0.5	0.1	1.5	0.3	1.0	0.0	0.4	0.7	0.4	4.9
Water 5 °C	0.5	0.1	1.3	0.3	0.9	0.0	0.4	0.5	0.3	4.2
Birch chip screenings										
0.1 M NaCl 60 °C	0.8	0.1	1.1	0.3	1.0	0.0	1.9	0.8	0.7	6.7
Water 60 °C	0.7	0.1	0.9	0.2	0.8	0.0	1.5	0.7	0.6	5.5
0.1 M NaCl 5 °C	0.7	0.1	1.0	0.2	1.2	0.0	1.7	0.7	0.8	6.3
Water 5 °C	0.8	0.1	1.2	0.3	0.9	0.0	1.8	0.7	0.8	6.6

FT-IR absorbance was measured for each lignin sample and for SXS. Only the spectra of lignin samples precipitated by 0.1 M NaCl solution at 60 °C are presented in Figure 22. Bands associated with lignin were found at 1705, 1603, 1515, 1464, 1456, 1424, 1368, 1325, 1269, 1217, 1150, 1141, 1120 and 1033 cm^{-1} (Ibrahim et al. 2007; Derkacheva and Sukhov 2008; Malutan et al. 2008). Absorption bands of sulphur compounds in SXS were found at 1407, 1399, 1377, 1198, 1169, 1150, 1131, 1097, 1049 and 820, 689 and 571 cm^{-1} (Silverstein et al. 1991; Hase 1999; Xu and Braterman 2003). The sulphur bands were not found in the different lignin spectra and it was concluded that the lignin samples did not contain SXS after precipitating and washing.

Absorbance
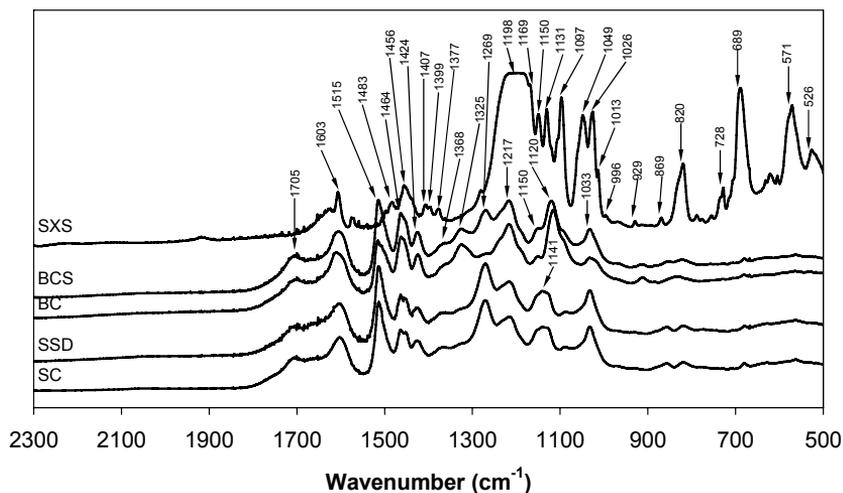
Figure 22. FT-IR absorbance spectra of precipitated lignin samples and SXS. Spectra of SXS: sodium xylenesulphonate, BCS: Nordic birch chip screenings, BC: Nordic birch chips, SSD: Norway spruce sawdust, SC: Norway spruce chips.

3.4 Energy, kraft pulp and chemicals from wood chip screenings [IV]

The amount of wood chip screenings produced in a pulp mill depends on the pulp wood consumption and the degree of screening loss per ton of wood. Two cases will be examined in the following text: one with low wood consumption per ton of wood and low screening loss (referred as Low) and the other with high wood consumption per ton of wood and high screening loss (referred as High). Based on Table 9 the amount of wood chip screenings varies between 20.6–68.0 o.d. kg/ADt. If the annual production of bleached pulp is 500 000 ADt the annual production of chip screenings can be calculated to be 10 303–34 021 tonnes calculated as dry wood.

3.4.1 Steam generation

According to Table 10 the amount of energy from chip screenings that can be converted to steam (8.4 MPa) is 0.30–0.99 GJ/ADt. If the annual production of pulp in a given mill is 500 000 ADt the heat generation varies from 150 000 GJ to 496 000 GJ, as seen in Table 17.

Table 17. Annual heat generation according to Fogelholm and Suutela 2000.

	Low	High	Unit
Wood to cooking	5.1	5.5	m^{3}sub/ADt
Screening loss	1	3	%
Heat to steam	0.30	0.99	GJ/ADt
Pulp production	500 000	500 000	ADt
Heat generation	150 000	496 000	GJ

Calculating the cost of generating steam from the boiler includes several factors: fuel consumption, raw material consumption, boiler feedwater treatment cost, feedwater pumping power, combustion air fan power cost, sewer charges for boiler blowdown, and costs for ash disposal, environmental emissions control, maintenance materials and labour. However the cost to generate steam is mainly the cost of fuel, comprising almost 90% of the total costs (Ryti 1987; Kumana 2003).

However, this fuel cost, consists of the cost of the wood material used for pulp production. The proportion of roundwood and sawmill chips (purchased chips) in pulp production and their prices has a major influence on the cost of fired chip screenings. In this study, wood furnish is comprised of 70% roundwood and 30% sawmill chips. According to [Paper IV] the annual profit for generating steam from chip screenings instead of using as *e.g.* landfill will range from 0.11–0.34 M€.

3.4.2 Production of bleached sawdust kraft pulp

Sawdust pulp is usually cooked in a separate digester system and blended with hardwood pulps prior to washing and bleaching (Tveit et al. 2006) and therefore the manufacturing costs of bleached sawdust pulp are estimated from hardwood kraft pulp production data. The costs can be estimated to be distributed according to Table 18 (Kotajärvi 2006).

Table 18. The cost factor distribution of kraft pulp, production 500 000 t/a according to Kotajärvi 2006.

Cost factor, %	Incl. Capital costs	Excl. capital costs
Capital costs	36	-
Wood raw material	31	48.4
Other production materials and services	11	17.2
Chemicals	8	12.5
Maintenance materials	5	7.8
Other costs	5	7.8
Labour and administration	3	4.7
Energy	1	1.6

The roundwood consumption of producing bleached hardwood kraft pulp is roughly 3.78 m^3/ADt (Fogelholm and Suutela 2000) and the price of hardwood roundwood is 33 €/m^3 (Metla 2008). The cost of hardwood raw material is then around 125 €/ADt and the total production cost of bleached sawdust pulp excluding capital costs will be approximately 325 €/ADt [Paper IV]. The production costs of bleached sawdust kraft pulp are calculated according to [Paper IV] and the annual profit for this mill will range from 1.55–5.10 M€, as seen in Table 19.

Table 19. Amount of different sawdust pulp grades produced annually and the profit from bleached sawdust kraft pulp.

Pulp grade	Yield, %	Low, ADt	High, ADt
Unbleached	46–48	5 300–5 500	17 300–18 100
Bleachable grade	43–45	4 900–5 200	16 300–17 000
Bleached	38.7–40.5	4 400–4 600	14 600–15 300
Production cost, 10^6 €		0.88	2.91
Selling price, 10^6 €		2.43	8.01
Profit, 10^6 €		1.55	5.10

According to the calculations for steam (Chapter 3.2.1) and bleached sawdust kraft pulp (Table 19) it is almost 15 times more profitable to produce bleached kraft pulp than generate steam from wood chip screenings if capital costs are excluded.

3.4.3   Chemical composition

The chemical composition of the studied raw materials was determined. When the annual production of bleached kraft pulp is

500 000 ADt the amount of o.d. wood chip screenings varies from 10 300–34 000 tonnes and the available wood constituents can be presented in Table 20.

Table 20. Annual amount of wood constituents that can be utilised from chip screenings. Ara: arabinose, Xyl: xylose, Gal: galactose, Man: mannose, Rha: rhamnose, GlcA: Glucuronic acid: 4-O-Me-GlcA: 4-O-methyl glucuronic acid, GalA: galacturonic acid, Glc: glucose.

t/a	Spruce/pine chip screenings		Pine chip screenings	
	Low	High	Low	High
Lignin	3 610	11 910	2 980	9 840
Cellulose	4 520	14 910	4 430	14 630
Ara	130	410	190	640
Xyl	400	1 320	560	1 840
Gal	250	830	410	1 360
Man	790	2 600	840	2 780
Rha	30	90	30	90
GlcA	10	30	10	20
4-O-Me-GlcA	60	200	80	250
GalA	150	510	180	600
Glc	260	850	310	1 030
Hemicelluloses total	2 080	6 840	2 610	8 610
Extractives	110	370	150	950

3.4.4   Ethanol production

In the following calculation, the maximum theoretical amount of ethanol that can be produced from wood chip screenings using cellulose, hexoses and pentoses is applied. The gross price of fuel ethanol (0.38 €/l) and the wood cost (33 €/m^3 for HW and 35 €/m^3 sob) are taken from [Paper IV]. The additional production costs are calculated according to Galbe and Zacchi (2002). The calculations are presented in Table 21.

Table 21. Annual ethanol production from wood chip screenings according to Galbe and Zacchi 2002. S/PCS: spruce/pine chip screenings, PCS: pine chip screenings, SSF: simultaneous saccharification and fermentation.

	S/PSC		PCS		
	Low	High	Low	High	Units
Carbohydrates	6 600	21 750	7 040	23 240	t/a
Ethanol	2 996 000	9 892 000	3 202 000	10 572 000	l/a
Gross price	0.38	0.38	0.38	0.38	€/l
Gross revenue	1.14	3.75	1.21	4.01	M€
Costs					
Raw material	0.306	0.306	0.286	0.286	€/l
Raw material handling	0.005	0.005	0.005	0.005	€/l
Pretreatment	0.042	0.042	0.042	0.042	€/l
SSF	0.138	0.138	0.138	0.138	€/l
Filtration	0.021	0.021	0.021	0.021	€/l
Distillation, evaporation	0.18	0.18	0.18	0.18	€/l
Product storage	0.005	0.005	0.005	0.005	€/l
Maintenance, labour, insurance	0.032	0.032	0.032	0.032	€/l
Lignin	-0.079	-0.079	-0.079	-0.079	€/l
Evaporation residue	-0.026	-0.026	-0.026	-0.026	€/l
CO_2	-0.005	-0.005	-0.005	-0.005	€/l
Total costs	0.619	0.619	0.599	0.599	€/l
	1.85	6.12	1.92	6.34	M€
Net profit	-0.72	-2.37	-0.71	-2.33	M€

Due to the high price of wood raw material delivered to pulp mills in the Nordic countries and the low price of fuel ethanol it is, according to our estimation, not economically feasible to produce ethanol from wood chip screenings even with the maximum theoretical conversion.

3.4.5 Production of bio-based chemicals

For example, succinic acid is used as a precursor of many industrially important chemicals, such as adipic acid, 1,4-butanediol, tetrahydrofuran and succinate salts, and is produced by microbial fermentation (Song and Lee 2006). In 1999 more than 15 000 tonnes of succinic acid was sold (Zeikus et al. 1999). Succinic acid for industrial use is predominately produced from petrochemical processes from butane through maleic anhydride, whereas food-grade succinic acid is produced through older fermentation and separation technology. Both routes are costly and this has limited use to specialised areas

(Meynial-Salles et al. 2008). However, the market potential in 2004 for products based on succinic acid was estimated to be more than 270 000 tonnes per year including 1,4-butanediol, tetrahydrofuran, γ-butyrolactone, adipic acid, *N*-methylpyrrolidone and linear aliphatic esters (Willke and Vorlop 2004). Succinic acid is sold at the price of 4.0–6.2 €/kg depending on its purity and the manufacturing costs of succinic acid are dependent on productivity and yield, raw material costs and recovery method, and are about 1.5 €/kg tonne/year level (Zeikus et al. 1999). Succinic acid can be produced from glucose with 91% (w/w) yield on glucose (Lee et al. 1999) thus the production cost economy of succinic acid from wood chip screenings can be calculated according to Table 22. It should be noted, that there are of course other sources of glucose, such as starch plants (starch, inulin, carbohydrates and cellulose) and sugar beets and sugar cane (sucrose). These sources of glucose are not studied, since the focus of the study is the utilisation of wood chip screenings.

Table 22. Succinic acid production from wood chip screenings. S/PCS: spruce/pine chip screenings, PCS: pine chip screenings.

| | S/PCS | | PCS | | |
	Low	High	Low	High	Units
Cellulose	4 520	14 910	4 430	14 630	t/a
Glucose from hemicelluloses	260	850	310	1 030	t/a
Glucose total	4 780	15 760	4 740	15 660	t/a
Succinic acid from glucose	4 340	14 340	4 320	14 250	t/a
Production costs	1.5	1.5	1.5	1.5	€/kg
	6.52	21.51	6.47	21.38	M€
Selling price	4.0	4.0	4.0	4.0	€/kg
	17.38	57.37	17.26	57.00	M€
Net profit	10.86	35.86	10.79	35.63	M€

The profit of producing succinic acid from wood chip screenings ranges from 10 M€ up to 35 M€, which is substantially higher in comparison to heat generation or bleached kraft pulp production as well as ethanol fuel production. Commercialisation of new low-cost approaches would significantly increase the market demand for succinic acid and its derivatives. This suggests that if the production

capacity of succinic acid of one mill varies between 4 300–14 300 tonnes per year, some 20 mills using close to maximum capacity could supply the estimated market potential. The current price range from 4.0–6.2 €/kg would probably become narrower and an average price per kg will probably be closer to 4 €/kg than 6.2 €/kg in a new market situation. However, if the selling price of is dropped down to 2 €/kg the profit excluding capital costs is around 2–7 M€, *i.e.* the profit is 5 times lower compared to 4 €/kg selling price. Since the production cost is about 1.5 €/kg it still is profitable on this basis. In addition, if investments in production facilities or refineries are needed, the profitability might not be as high as calculated.

3.5 Sawdust reinforcement fibre (RIF) pulp [V]

The aim of this work was to add bleached unrefined and refined sawdust kraft pulp into bleached mechanical pulps in order to examine whether sawdust pulp can reinforce mechanical pulp based papers. Also, economic calculations were done to estimate the cost of bleached long fibre reinforcement kraft pulp, bleached mechanical pulp, and bleached sawdust kraft pulp.

Properties of the different pulp fibres are listed in Table 22. TMP fibres were longer that PGW fibres. In addition, unrefined and refined sawdust kraft pulp fibres were longer than PGW fibres. The fibre width of TMP and sawdust kraft pulps was higher than that of PGW. TMP fibre walls were thicker than the rest of the studied fibres. PGW and sawdust kraft pulps contained considerable more fibres per unit weight than TMP. Additionally, their fines content was higher than TMP.

Table 23. Properties of TMP, PGW, bleached sawdust kraft pulp and refined sawdust kraft pulp fibres.

	TMP			PGW			BSDKP			BSDKP R (°SR 33)		
Fibre length (mm)	1.67	±	0.04	0.84	±	0.03	1.17	±	0.03	1.00	±	0.04
Fibre width (μm)	28.56	±	0.42	22.59	±	0.51	28.42	±	0.28	26.72	±	0.22
Fibre wall (μm)	8.05	±	0.22	6.58	±	0.12	6.96	±	0.28	6.85	±	0.14
Curl (%)	15.99	±	0.50	15.03	±	0.47	9.06	±	0.35	8.38	±	0.21
Coarseness (mg/m)	0.27	±	0.03	0.17	±	0.01	0.17	±	0.00	0.15	±	0.00
10^6 fibres/g	4.35	±	0.39	14.63	±	0.98	11.97	±	0.10	17.21	±	0.26
Fines (%)	20.32	±	0.75	34.81	±	1.47	39.62	±	1.13	45.30	±	0.82

Mean length-weighted fibre length. BSDKP: bleached sawdust kraft pulp, BSDKP R: bleached and refined (°SR 33) sawdust kraft pulp.

The drainage resistance of pure PGW pulp was higher than that of pure TMP pulp because PGW pulp contains more fines which retain water, as seen at 0% sawdust addition in Figure 23. The drainability of the mechanical pulp furnishes increased with the addition of both unrefined and refined sawdust pulp. An interesting feature was observed when adding 5–30% unrefined sawdust kraft pulp into the mechanical pulps. The drainability was lower compared with adding refined sawdust pulp even if the fines content of the unrefined sawdust pulp was lower than that of refined sawdust pulp.
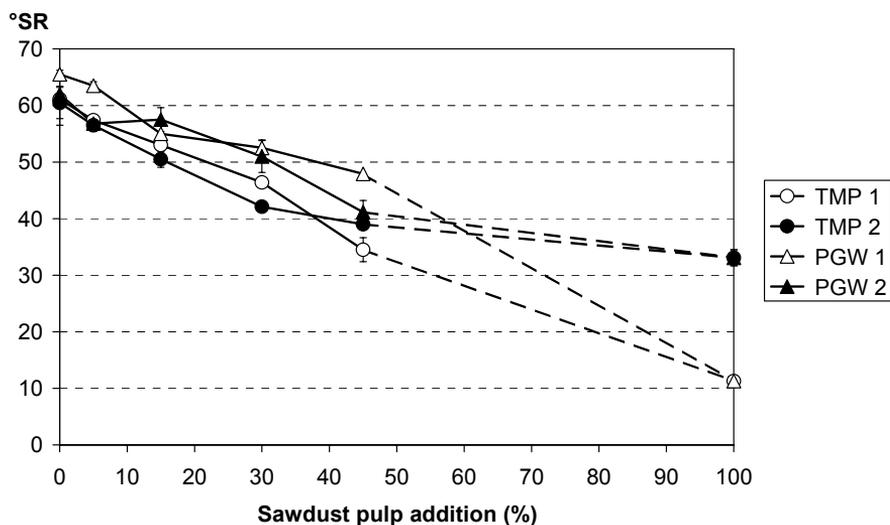
Figure 23. Drainability of the different pulp furnishes. TMP 1: Bleached thermomechanical pulp blended with bleached, unrefined sawdust kraft pulp, TMP 2: Bleached thermomechanical pulp blended with bleached, refined sawdust kraft pulp, PGW 1: Bleached pressurised groundwood pulp blended with bleached, unrefined sawdust kraft pulp, PGW 2: Bleached pressurised groundwood pulp blended with bleached, refined sawdust kraft.

The bulk of TMP and PGW based papers can be seen in Figure 24. The bulk of TMP and PGW pulp furnishes was high and remained more or less constant regardless of the amount of unrefined sawdust pulp added into the pulp furnishes. This was due to the high bulk of unrefined sawdust pulp. In contrast to unrefined sawdust pulp, the refined sawdust pulp has a lower bulk and therefore the increased amount of refined pulp in mechanical pulps decreased the bulk. However, the bulk of the different mechanical pulp furnishes did not decrease clearly until 30% of refined sawdust pulp was added.
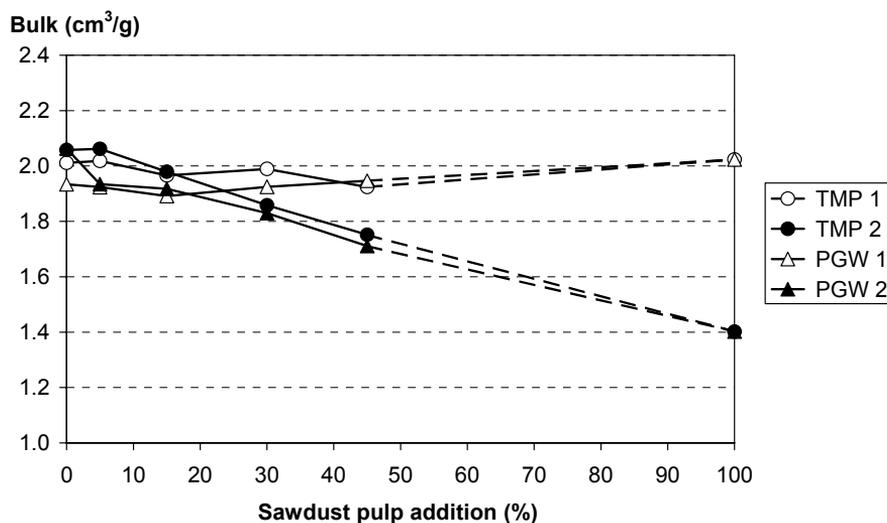
Bulk (cm³/g)

Figure 24. Bulk of the different pulp furnishes.

TMP had higher tear strength than PGW pulp because TMP contained longer fibres, see Figure 25. Tear index depends on the fibre length and its strength. It has been shown that tear strength is increased with increasing fibre length (Mohlin 1989; Seth 1990; Retulainen 1996). Tear index of TMP remained almost unchanged when unrefined sawdust pulp was added because tear strength of unrefined sawdust pulp was at same level as TMP. Addition of refined sawdust pulp to pure TMP decreased the tear strength of TMP furnishes only slightly.
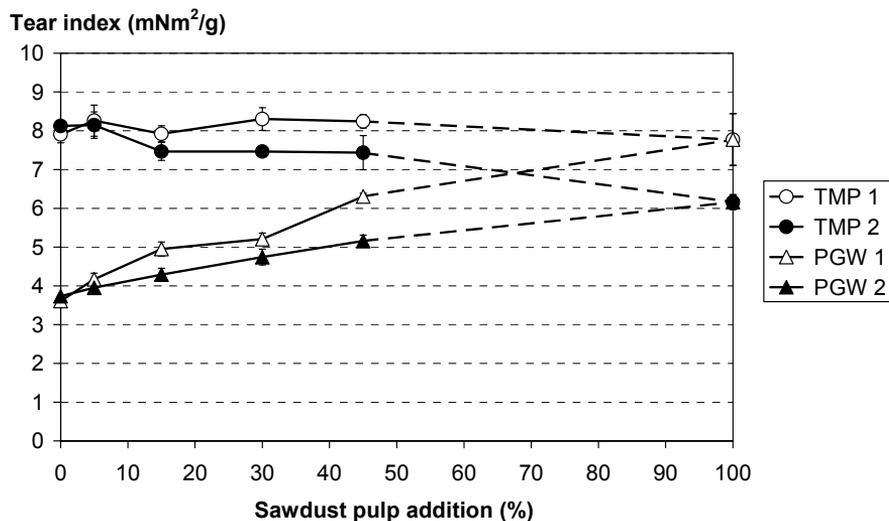
Tear index (mNm^2/g)

Figure 25. Tear index of the different pulp furnishes.

Tear strength of PGW pulp furnishes increased with increased addition of both unrefined and refined sawdust pulp. Unrefined sawdust pulp fibres were longer than refined sawdust pulp fibres. Also, the coarseness of unrefined sawdust pulp was higher. Coarser fibres improve the tear strength (Seth and Page 1988; Yu 2001). Therefore the addition of unrefined sawdust pulp into the PGW pulp furnishes showed higher increase in tear strength.

There were no significant differences in tensile strength between the TMP and PGW pulps, as reported earlier (Lindholm 1981). The addition of unrefined sawdust pulp into the mechanical pulp furnishes did not decrease the tensile strength although the tensile strength of unrefined sawdust pulp was lower than that of TMP and PGW which is illustrated in Figure 26. In fact, the tensile strength of the mechanical pulp furnishes increased slightly when 5–15% unrefined sawdust pulp was added.

Tensile strength of the mechanical pulp furnishes increased with increased amount of refined sawdust pulp even though the fibres in the sawdust pulp were relatively short compared to conventional softwood reinforcement pulp fibres. Refining of the sawdust pulp fibres improved the tensile properties. During refining external and internal fibrillation occurs, the sawdust pulp fibres, collapse, are cut and fines are generated (Page 1989; Paavilainen 1993). Because of this,

sawdust pulp fibres became more flexible which made the formation of fibre-fibre bonds easier. Additionally, due to increased fines content of the sawdust pulp the tensile strength was increased (Hartman 1985; Page 1985).
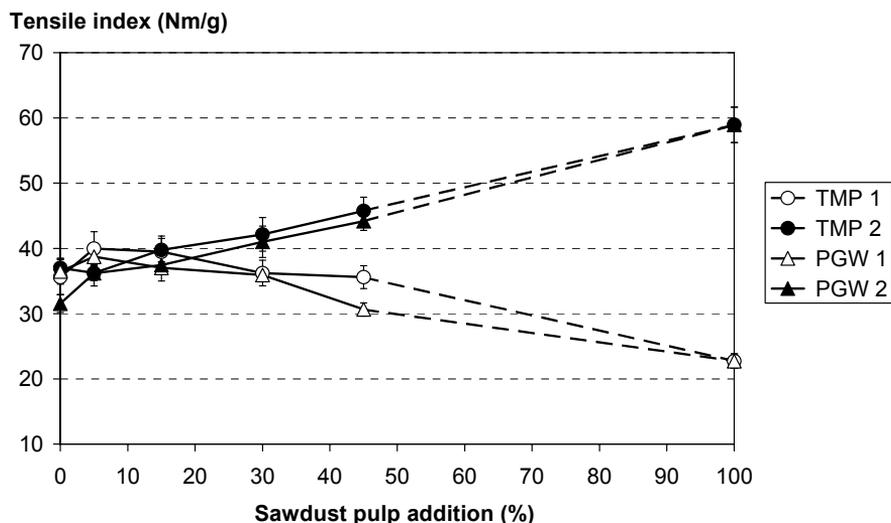

Figure 26. Tensile index of the different pulp furnishes.

The main cost factor of manufacturing softwood reinforcement kraft pulp excluding capitals costs is the cost of wood. The cost of wood excluding capital costs is around 48.6%, as seen in Table 22 (Diesen 1998). Other costs are chemicals, energy, operating materials, services, maintenance materials, personnel, administration, etc. The price of Norway spruce roundwood is approximately 34 €/solid m³ (Metla 2009) and the wood consumption of RIF pulp is 5.45 solid m³/admt. The cost of roundwood is then around 185 €/admt the total production cost of bleached RIF kraft pulp excluding capital costs will be approximately 380 €/admt, which is illustrated in Table 24. The calculated cost is relatively close to the value reported earlier (Pineault 2006).

Table 24. The cost factor distribution of softwood reinforcement fibre kraft pulp according to Diesen 1998.

Cost factor	Incl. capital costs, %	Excl. capital costs, %	€/admt
Wood	31	48.6	185.4
Chemicals	7.9	12.4	47.2
Energy	0.7	1.1	4.2
Operating materials, services	10.7	16.8	64.0
Maintenance materials	5.2	8.2	31.1
Personnel and administration	3.3	5.2	19.7
Others	5	7.8	29.9
Capital costs	36.2	-	-
Total	100	100	381.5

The calculated cost factors for mechanical pulp are presented in Table 25. In this case too, the main cost factor is the cost of wood. Other cost factors are, *e.g.*, chemicals, packing materials, energy, operating materials, maintenance materials, personnel and administration (Diesen 1998). The price of wood is approximately 34 €/solid m^3 (Metla 2009) and the wood consumption is 2.70 solid m^3/admt. The total production cost of bleached mechanical pulp is 280 €/admt which is close to the reported values of 250–280 €/t (Honkasalo 2004).

Table 25. The cost factor distribution of mechanical pulp made from softwood according to Diesen 1998.

Cost factor	Incl. capital costs, %	Excl. capital costs, %	€/admt
Raw material (wood)	23.8	32.7	87.6
Chemicals	6.7	9.2	24.7
Packing materials	2.0	2.7	7.4
Energy	13.2	18.1	48.6
Operating materials	3.6	4.9	13.3
Maintenance materials	5.5	7.6	20.3
Personnel and administration	13.7	18.8	50.4
Others	4.3	5.9	15.8
Capital costs	27.2	-	-
Total	100	100	280.4

Finally, the cost factors for bleached sawdust kraft pulp are calculated and they can be seen in Table 26. The price for sawdust is 6.1 €/loose m^3 (Ylitalo 2006) and the wood consumption is 15.2 loose m^3/admt. Therefore, the cost wood in the production of bleached sawdust kraft pulp is 93 €/admt, as seen in Table 26. The rest of the production costs are taken from Table 22 even though their value might be overestimated.

Table 26. The cost factor distribution of sawdust kraft pulp.

Cost factor	Excl. capital costs, €/admt
Wood	92.7
Chemicals	47.2
Energy	4.2
Operating materials, services	64.0
Maintenance materials	31.1
Personnel and administration	19.7
Others	29.9
Capital costs	-
Total	288.8

According to Tables 24 and 26 bleached sawdust kraft pulp is 93 €/admt cheaper than bleached softwood reinforcement kraft pulp. In addition, the production cost of bleached sawdust kraft pulp excluding capital cost is almost the same as the production cost of bleached mechanical pulp.

4 Concluding remarks

Sawdust and wood chip screenings have been regarded as waste material which is usually combusted in a mill or in the worst case used as landfill. The annual production of these finely divided wood materials is considerable and there are various applications where sawdust and wood chip screenings can be utilised.

The traditional ways of utilising sawdust-like materials are steam and energy conversion and kraft pulp production. Steam and heat are always needed in the pulp and paper mills but the described process alternatives are relatively profitable although the wood material needed is comparatively expensive. For example, the production of sawdust kraft pulp is more profitable than heat generation.

The production capacity of sawdust kraft pulp in a certain digester can be increased by introducing an impregnation stage. At the same time, pulp properties of the produced pulp will also be improved. Sawdust kraft pulp from softwood can be used for many purposes and it can replace birch kraft pulp in several applications. It can even be used as reinforcement fibre pulp in mechanical pulp based paper formulations.

The sawdust-like wood material can alternatively be treated with a hydrotropic solution and the lignin which is extracted does not contain any or only negligible amounts of sulphur compounds. This lignin is a very attractive raw material for biofuel production and feedstock for chemicals and materials.

The finely divided wood material can also be converted into ethanol fuel but the wood material would have to be much cheaper than it is nowadays in order to make the ethanol fuel production profitable. There are also challenges concerning the conversion of pentose sugars into ethanol.

Due to the fact that wood material is expensive in the Nordic countries the production of high value added chemicals is economically the best choice for utilising wood chip screenings and sawdust. However, case-specific investment cost analyses must be done before decision-making.

5 Acknowledgements

6 References

Aarne, M. (2008) Forest industries. In: Finnish Statistical Yearbook of Forestry 2008. Ed. Peltola, A. Finnish Forest Research Institute, Helsinki, Finland. pp. 299–322.

Adler, E. (1977) Lignin Structure – Past, Present and Future. Wood. Sci. Technol. 11(3): 169–218.

Akhtaruzzaman, A.F.M., Virkola, N.-E. (1979a) Influence of Chip Dimensions in Kraft Pulping, Part III: Effect on Delignification and a Mathematical Model for Predicting the Pulping Parameters. Pap. Puu. 61(11): 737–751.

Akhtaruzzaman, A.F.M., Virkola, N.-E. (1979b) Influence of Chip Dimensions in Kraft Pulping, Part IV: Effect on Screened Pulp Yield and Effective Alkali Consumption: Predictive Mathematical Models. Pap. Puu 61(12): 805–814.

Alakangas, E. Properties of wood fuels used in Finland. Technical Research Centre of Finland, VTT Processes, Project report PRO2/P2030/05 (Project C5SU00800), Jyväskylä, Finland, 2005. 90 pp.

Alén, R. (1990) Conversion of cellulose-containing materials into useful products. In: Cellulose Sources and Exploitation - Industrial Utilization, Biotechnology and Physico-Chemical Properties. Eds. Kennedy, J.F., Phillips, G.O., Williams, P.A. Ellis Horwood, New York (NY), USA. pp. 453–464.

Alén, R. (2000) Basic chemistry of wood delignification. In: Papermaking Science and Technology, Book 3, Forest Products Chemistry. Ed. Stenius P. Fapet Oy, Helsinki, Finland. pp. 58–104.

Andelin, J. and others. Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp. Background Paper [OTA-BP-O-54], U.S. Congress, Office of Technology Assessment, Washington (DC), USA, 1989. 74 pp.

Andersson von, A., Erickson, M., Fridh, H., Miksche, G. (1973) On the Structure of the Bark Lignins of Hardwoods and Softwoods. Holzforschung 27(6): 189–193.

Anon. (2004) The biggest and the best environmental and energy equipment available today. FiberSpectrum 3(2): 8–11.

Arends, G.J., Donkersloot-Shouq S.S. An overview of possible uses of sawdust. TOOL, Amsterdam, The Netherlands, 1985. 197 pp.

Aurell, R., Stockman, L., Teder, A. (1958) Flisens impregnering vid sulfitkokning. Del 2. Sven. Papperstidn. 61(21): 937–944.

Axegård, P., Backlund, B., Warnqvist, B. (2002) The Eco-Cyclic pulp mill: Focus on closure, energy-efficiency and chemical recovery development. Pulp Pap. Can. 103(5): T116–T119.

Backman, M., de Leon, J.P.G. (1998) Pulp and paper properties of four-year old eucalyptus trees for early species selection. In: Proceedings of the 52nd Appita Annual General Conference, Vol 1., Brisbane, Australia. pp. 7–13.

Bail, C.M. (1979) Sawdust pulping continues to grow; technology improves yield, strength. Pulp Pap. 53(2): 105–109.

Balasubramanian, D., Srinivas, V., Gaikar, V.G., Sharma, M.M. (1989) Aggregation Behavior of Hydrotropic Compounds in Aqueous Solution. J. Phys. Chem. 93(9): 3865–3870.

Bausch, H., Hartler, N. (1960) Determination of Chip Dimensions. Sven. Papperstidn. 63(10): 319–326.

Bergström, D., Israelsson, S., Öhman, M., Dahlqvistd, S.-A., Gref, R., Boman, C., Wästerlund I. (2008) Effects of raw material particle size distribution on the characteristics of Scots pine sawdust fuel pellets. Fuel Process. Technol. 89(12): 1324–1329.

Björklund, L. Bark på massaved – en studie över barkhalten i travar med massaved. The Swedish Timber Measurement Council (VMR) virkesmätning och redovisning, Reports, Sundsvall, Sweden, 2004. 17 pp.

Bublitz, W.J., Yang, T.Y. (1975) Pulping characteristics of Douglas-fir sawdust. Tappi 58(3): 95–99.

Cannel, E. (1999) Pulp Screening Advancements Reduce Shives, Boost Quality. Pulp Pap. 73(7): 76–78.

Clayton, D., Easty, D., Einspahr, D., Lonsky, W., Malcolm, E., McDonough, T., Schroeder, L., Thompson, N. (1989) Process Variables. In: Pulp and Paper Manufacture, Volume 5, Alkaline Pulping. Eds. Grace, T.M., Leopold, B., Malcolm, E.W. Joint Textbook Committee of the Pulp and Paper Industry (TAPPI/CPPA), Atlanta (GA), USA. pp. 74–113.

Crocker, M., Crofcheck, C. (2006), Biomass Conversion to Liquid Fuels and Chemicals. Energeia 17(6): 1–3.

Derkacheva, O., Sukhov, D. (2008) Investigation of Lignins by FTIR Spectroscopy. Macromol. Symp. 265(1): 61–68.

Dhamodaran, T.K., Gnanaharan, R., Sankara Pillai, K. Bamboo for Pulp and Paper - A State of the Art Review With Annotated Bibliography. International Network for Bamboo and Rattan (INBAR), Beijing, China, 2003. 208 pp.

Dhamodaran, T.K., Gnanaharan, R. (2006) En economical treatment schedule for boron impregnation of *Eucalyptus grandis* wood: Commercial trial of partially dried material. Holz Roh. Werkst. 64(1): 80–81.

Diesen, M. (1998) Cost structure and management accounting. In: Papermaking Science and Technology, Book 1, Economics of the Pulp and Paper Industry. Ed. Diesen, M. Fapet Oy, Helsinki, Finland. pp. 101–125.

Donaldson, L.A. (2001) Lignification and lignin topochemistry — an ultrastructural view. Phytochemistry 57(6): 859–873.

Duchesne, I., Wilhemsson, L., Spånberg, K. (1997) Effects of in-forest sorting of Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) on wood and fibre properties. Can. J. For. Res. 27(5): 790–795.

Ekman, K.H., Fogelberg, B.C. (1966) Impregnation on Sulphate Cooking Studied by Means of Radioactive Sulphur. Pap. Puu 48(4a): 175–182.

Ekman, R., Holmbom, B. (1989) Analysis by gas chromatography of the wood extractives in pulp and water samples from mechanical pulping of spruce. Nord. Pulp Pap. Res. J. 4(1): 16–24.

Finnish Forest Industries Federation (2009) Annual and quarterly statistics, http://www.forestindustries.fi/tilastopalvelu/Tilastotaulukot/Annual/Forms/AllItems.aspx, accessed 3.6.2009.

Fogelholm, C.-J., Suutela, J. (2000) Heat and power co-generation. In: Papermaking Science and Technology, Book 6B, Chemical Pulping. Eds. Gullichsen, J., Fogelholm, C.-J. Fapet Oy, Helsinki, Finland. pp. B302–B335.

Friberg, S.E., Brancewicz, C. (1997) Hydrotropy. In: Surfactant Science Series, Volume 67, Liquid Detergents Ed. Lai, K.-Y. Marcel Dekker, New York (NY), USA. pp. 21–34.

Fuller, W.S. (1983) Chipping, Screening and Cleaning. In: Pulp and Paper Manufacture, Volume 1, Properties of Fibrous Raw Materials and their Preparation for Pulping. Eds. Kocurek, M.J., Stevens, C.F.B. Joint Textbook Committee of the Pulp and Paper Industry (TAPPI/CPPA), Atlanta (GA), USA. pp. 128–144.

Galbe, M., Zacchi, G. (2002) A review of the production of ethanol from softwood. Appl. Microbiol. Biotechnol. 59(6): 618–628.

Gold, V., Loening, K.L., McNaught, A.D., Sehmi, P. (eds.) Compendium of Chemical Technology: IUPAC recommendations. Blackwell Scientific Publications, Oxford, UK, 1987. pp. 121–122.

Graeme, R. (1997) Elk Falls continues pioneering work in mini-chip pulp production. Pulp Pap. Can. 98(10): 18–19.

Graeme, R. (2004) Ushering in a New Pulping Era. Pulp Pap. Int. 46(10): 38–39.

Grattapaglia, D. (2007) Forward Genomics in Eucalyptus: From Phenotypes to Genes Involved in Wood Formation. In: Proceedings of the 3rd ICEP International Colloquium on Eucalyptus Pulp, Vol 1., Belo Horizonte, Brazil. pp. 1–8.

Gullichsen, J. (1999) Fiber line operations. In: Papermaking Science and Technology, Book 6A, Chemical Pulping. Eds. Gullichsen, J., Fogelholm, C.-J. Fapet Oy, Helsinki, Finland. pp. A17–A243.

Hamelinck, C.N., Faaij, A.P.C. (2006) Outlook for advanced biofuels. Energy Policy 34(17): 3268–3283.

Hartler, N. (1962) Penetrerings- och diffusionsförhållandena vid sulfatkoket. Pap. Puu 44(7): 365–374.

Hartman, R.R. (1985) Mechanical treatment of pulp fibers for paper property development. In: Transactions of the Eighth Fundamental Research Symposium, Vol. 1., Papermaking Raw Materials, Oxford, England. pp. 413-442.

Hase, T. Tables for organic spectrometry. Otatieto, Helsinki, Finland 1999. 78 pp.

Hodgdon, T.K., Kaler, E.W. (2007) Hydrotropic solutions. Curr. Opin. Colloid Interface Sci. 12(3): 121–128.

Holmbom, B., Konn, J., Pranovich, A. (2005) What is the true yield of TMP and CTMP? What is lost in refining and bleaching? In:

Proceedings of the IMPC International Mechanical Pulping Conference, Oslo, Norway. pp. 98–101.

Honkasalo, J. Behaviour of Different Furnish Mixtures in Mechanical Printing Papers, Doctoral thesis, Helsinki University of Technology, Espoo, Finland, 2004. 134 pp.

Huber, G.W., Dumesic, J.A. (2006) An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. Catal. Today 111(1-2): 119–132.

Hultholm, T. Impregnation behaviour of the active ions in the kraft process, Doctoral Thesis, Åbo Akademi University, Turku, Finland, 2004. 157 pp.

Hägglund, E. Chemistry of Wood. Academic Press Inc. Publishers, New York (NY), USA, 1951. 631 pp.

Häggblom-Ahnger, U., Komulainen, P. Kemiallinen metsäteollisuus II, Paperin ja kartongin valmistus. Ed. Seppälä, M.J. Opetushallitus, Helsinki, Finland, 2001. 280 pp.

Ibrahim, M.N.M., Yusof, N.N.M., Hashim, A. (2007) Comparison studies on soda lignin and soda-anthraquinone lignin. Malay. J. Anal. Sci. 11(1): 206–212.

Ingruber, O.V. (1989) Alkaline Digester Systems. In: Pulp and Paper Manufacture, Volume 5, Alkaline Pulping. Eds. Grace, T.M., Leopold, B., Malcolm, E.W. Joint Textbook Committee of the Pulp and Paper Industry (TAPPI/CPPA), Atlanta (GA), USA. pp. 140–180.

Irvine, J.E. (1966) The Bauer M&D Digester Applied to Sawdust Kraft Pulping. Pap. Puu 48(4a): 201–204.

Isomäki, O. (1970) Tutkimus sahanpurun perusominaisuuksista. Pap. Puu 52(9): 571–584.

Isotalo, I., Göttsching, L., Virkola, N.-E., Nordman, L. (1964a) The Preparation of Sawdust Sulphate Pulp and Its use in Printing Paper Manufacture I. Pap. Puu 46(3): 71–85.

Isotalo, I., Göttsching, L., Virkola, N.-E., Nordman, L. (1964b) The Preparation of Sawdust Sulphate Pulp and Its use in Printing Paper Manufacture II. Pap. Puu 46(4a): 237–248.

Jensen, W. (1948) On surface waste in the production of Birch plywood. Finn. Pap. Timber J. 30(23): 425–429.

Joshi, R.C., Bist, D.P.S., Jangalgi, N.R., Kaul, S.S. (1982) Pulping Studies on Sawdust. Indian Pulp Pap. 37(2): 12–19.

Kamm, B. (2007) Production of Platform Chemicals and Synthesis Gas from Biomass. Angew. Chem. Int. Ed. 46(27): 5056–5058.

Kamm, B., Kamm, M. (2004) Principles of biorefineries. Appl. Microbiol. Biotechnol. 64(2): 137–145.

Korpinen, R. Simulering och optimering av sågspånskok i laboratorieskala, M.Sc. Thesis, Åbo Akademi University, Turku, Finland, 2002. 87 pp.

Korpinen, R., Fardim, P. (2006) Characterisation of sawdust-like wood materials. In: Proceedings of the 9th EWLP European Workshop on Lignocellulosics and Pulp, Vienna, Austria. pp. 315–318.

Koskinen, K. (1999) Wood handling applications. In: Papermaking Science and Technology, Book 6A, Chemical Pulping. Eds. Gullichsen, J., Fogelholm, C.-J. Fapet Oy, Helsinki, Finland. pp. A328–A491.

Kotajärvi, S. Maailman kuitumarkkinat ja kuituraaka-aineen tutkimuksen näkymiä, Etelä-Karjalan ammattikorkeakoulun julkaisuja - Sarja A, Imatra, Finland, 2006. 44 pp.

Kovasin, K.K., Tikka, P.O. (1993) Low-Kappa Kraft Pulping and its Advantages. Pap. Puu 75(7): 491–497.

Kumana, J.D. A Best Practices Steam Technical Brief - How To Calculate The True Cost of Steam. U.S. Department of Energy Office of Industrial Technologies, Washington (DC), USA, 2003. 13 pp.

Kuznetsova, S.A.; Levdansky, V.A.; Kuznetsov, B.N.; Shchipko, M.L.; Ryazanova, T.V.; Kovalchik, N.M. (2005) Obtaining Tanning Agents, Dyes, and Enterosorbents from Bast of a Birch Bark. Chem. Sustainable Dev. 13(3): 399–407.

Lee, P.C., Lee, W.G., Kwon, S., Lee, S.Y., Chang, H.N. (1999) Succinic acid production by *Anaerobiospirillum succiniciproducens*: effects of the H_2/CO_2 supply and glucose concentration. Enzyme Microb. Technol. 24(8–9): 549–554.

Liiri, J. Sahanpurun keittoprosessin ja sen lämpötilasäädettävyyden tutkiminen jatkuvatoimisella Enso-Bauer M & D –keittimellä, M.Sc. Thesis, Lappeenranta University of Technology, Lappeenranta, Finland, 1979. 70 pp.

Lindholm, C.-A. (1981) Comparison of some papermaking properties of groundwood, pressure groundwood and thermomechanical pulp by means of artificial blends of pulp fractions. Part 3. The fibre fractions. Pap. Puu 63(8): 487–497.

Lukkari, T. Puusta jalosteeksi. Metsäteollisuus ry, Suomen Metsäyhdistys ry, Helsinki, Finland, 1998. 75 pp.

Lundquist, K., Lundgren, R. (1972) Acid Degradation of Lignin. Part VII. The Cleavage of Ether Bonds. Acta Chem. Scand. 26(5): 2005–2023.

Lönnberg, B. 13-71 VII Suursaanto- ja sahanpurumassat paperin raaka-aineina. Puumassa- ja paperiteollisuuden täydennyskoulutuspäivät, Osa III. Insinöörijärjestöjen Koulutuskeskus – Ingenjörsorganisationernas Skolningscentral, Helsinki, Finland, 1971. 15 pp.

Lönnberg, B., Backman, M., Ebeling, K., Henrickson, K., Laxén T. (1995) Impregnation-Depolymerisation-Extraction (IDE) pulping of wood and nonwood raw materials. In: proceedings of the PTS-TUD Symposium Chemical and Mechanical Pulp Technology '95, Dresden, Germany. pp. 14–14E.

MacLeod, J.M., Kingsland, K.A. (1990) Kraft-AQ pulping of sawdust. Tappi J. 73(1): 191–193.

Malkov, S. Studies on Liquid Penetration into Softwood Chips - Experiments, Models and Applications, Doctoral Thesis, Helsinki University of Technology, Espoo, Finland, 2002. 64 pp.

Malkov, S., Tikka, P., Gullichsen, J. (2001) Towards complete impregnation of wood chips with aqueous solutions. Part 3. Black liquor penetration into pine chips. Pap. Puu 83(8): 605–609.

Malkov, S., Kuzmin, V.A., Baltakhinov, V.P., Tikka, P. (2002) Efficiency of chip presteaming - result of heating and air escape processes. Nord. Pulp Pap. Res. J. 17(4): 420–426.

Malutan, T., Nicu, R., Popa, V.I. (2008) Lignin modification by epoxidation. BioRes. 3(4): 1371–1376.

Marcoccia, B., Prough, J.R., Engström, J., Gullichsen, J. (1999) Continuous cooking applications. In: Papermaking Science and Technology, Book 6A, Chemical Pulping. Eds. Gullichsen, J., Fogelholm, C.-J. Fapet Oy, Helsinki, Finland. pp. A512–A570.

Markham, L.D. (1984) Horizontal tube reactors can be answer to many pulping problems. Pulp Pap. 58(2): 105–107.

Martikainen, P. (2002) Puutuoteteollisuus. In: Tapion taskukirja. Ed. Hyvämäki, T. Metsätalouden kehittämiskeskus Tapio & Metsälehti Kustannus, Helsinki, Finland. pp. 537–544.

Matsumara, J., Booker, R.E., Donaldson, L.A., Rridoutt, B.G. (1998) Impregnation of radiata pine wood by vacuum treatment:

Identification of flow paths using fluorescent dye and confocal microscopy. IAWA J. 19(1): 25–33.

Matsumara, J., Booker, R.E., Ridoutt, B.G., Donaldson, L.A., Mikajiri, N., Matsunaga, H., Oda, K. (1999) Impregnation of radiata pine wood by vacuum treatment II: effect of pre-steaming on wood structure and resin content. J. Wood Sci. 45(6): 456–462.

McKee, R.H. (1943) Recovery of Cellulose and Lignin from Wood. U.S. Patent 2,308,564.

McKee, R.H. (1946) Use of Hydrotropic Solutions in Industry. Ind. Eng. Chem. 38(4): 382–384.

Metla (Finnish Forest Research Institute) (2008) Puun hinnat kuukausittain, http://www.metla.fi/cgi-bin/tilasto/mo/kk-hinnat-alue.cgi, accessed 17.01.2008.

Metla (Finnish Forest Research Institute) (2009) Puun hinnat kuukausittain, http://www.metla.fi/cgi-bin/tilasto/mo/kk-hinnat-alue.cgi, accessed 10.02.2009.

Meynial-Salles, I., Dorotyn, S., Soucaille, P. (2008) A New Process for the Continuous Production of Succinic Acid From Glucose at High Yield, Titer, and Productivity. Biotechnol. Bioeng. 99(1): 129–135.

Miele, J.J., Marois, M., Chasse, R.F., Chamblee, J.W., Weston, J.D., Prough, J.R. (2001) Method for pulping sawdust. U.S. Pat. 6,325,888 B1.

Mimms, A., Kocurek, M.J., Pyatte, J.A., Wright, E.E. Eds. Kraft Pulping - A compilation of Notes. Tappi, Atlanta (GA), USA, 1995. 181 pp.

Mohlin, U.-B. (1989) Fibre bonding ability - a key pulp quality parameter for mechanical pulps to be used in printing papers. In: Proceedings of the IMPC International Mechanical Pulping Conference, Helsinki, Finland. pp. 49–57.

Mörseburg, K., Hultholm, T., Lundin, T., Lönnberg, B. (1999) Experiences with the Kajaani FiberLab Analyzer in determining morphological characteristics of mechanical and chemical pulps. In: Proceedings of the 5th PTS-Symposium Papierfaserstoff-Technik, Dresden, Germany. pp. 13-1–13-11.

Paavilainen, L. (1993) Conformability - flexibility and collapsibility - of sulphate pulp fibres. Pap. Puu 75(9–10): 689-702.

Page, D.H. (1985) The mechanism of strength development of dried pulps by beating. Svensk Papperstidn. 88(3): R30–R35.

Page, D.H. (1989) The beating of chemical pulps – the action and the effect. In: Transactions of the Ninth Fundamental Research Symposium, Vol. 1., Fundamentals of Papermaking, Cambridge, England. pp. 1–38.

Paranyi, N.I., Rabinovitch, W. (1955) Determination of Penetration Rate of Liquid Media in Wood Using a Quartz Spiral Balance. Part I. Water and an Air-dry Spruce Chip. Pulp Pap. Mag. Can. 56(3): 163–170.

Parham, R.A. (1983a) Ultrastructure and Chemistry. In: Pulp and Paper Manufacture, Volume 1, Properties of Fibrous Raw Materials and their Preparation for Pulping. Eds. Kocurek, M.J., Stevens, C.F.B. Joint Textbook Committee of the Pulp and Paper Industry (TAPPI/CPPA), Atlanta (GA), USA. pp. 35–45.

Parham, R.A. (1983b) Wood Variability. In: Pulp and Paper Manufacture, Volume 1, Properties of Fibrous Raw Materials and their Preparation for Pulping. Eds. Kocurek, M.J., Stevens, C.F.B. Joint Textbook Committee of the Pulp and Paper Industry (TAPPI/CPPA), Atlanta (GA), USA. pp. 55–65.

Pekkala, O. (1982) On the extended delignification using polysulphide or anthraquinone in kraft pulping. Pap. Puu 64(11): 735–744.

Pellikka, J., Saviharju, K. (1983) Kuoren ja puujätteen poltto. In: Puumassan valmistus, Suomen Paperi-insinöörien Yhdistyksen oppi- ja käsikirja II, Osa 2. Ed. Virkola, N.-E. Teknillisten tieteiden akatemia, Helsinki, Finland. pp. 1519–1582.

Pineault, D. (2006) Manufacturing Costs in the Global Market Pulp Sector. PaperAge 122(1): 20–22.

Procter, A.R., Chow, W.M. (1976) Simulated hardwood market kraft pulp from western red cedar sawdust. Tappi 59(2): 119–123.

Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick Jr., W.J., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., Tschaplinski, T. (2006) The Path Forward for Biofuels and Biomaterials. Science 311(5760): 484–489.

Raman, G., Gaikar, V. (2002) Extraction of Piperine from *Piper nigrum* (Black Pepper) by Hydrotropic Solubilization. Ind. Eng. Chem. Res. 41(12): 2966–2976.

Ramos, L.P. (2003) The Chemistry Involved in the Steam treatment of Lignocellulosic Materials. Quim. Nova 26(6): 863–871.

Rantasuo, P. (1976) Framställning av sågspånscellulosa med Enso-Bauer M&D-kokare. Norsk Skogind. 30(6): 186–188.

Rekunen, S., Jutila, E., Lähteenmäki, E., Lönnberg, B., Virkola, N.-E. (1980) Examination of reaction kinetics in kraft cooking. Pap. Puu 62(2): 80–90.

Ressel, J.B. (2006) Wood Yard Operations. In: Handbook of Pulp, Volume 1. Ed. Sixta, H. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2006. pp 69–107.

Retulainen, E. (1996) Fibre properties as control variables in papermaking. Part 1. Fibre properties of key importance in the network. Pap. Puu 78(4): 187–194.

Robertsén, L., Pekkala, O., Leminen, A. (1999) Impregnation of wood with white and black liquor. In: Proceedings of the 13th International papermaking conference – progress '99, Krakow, Poland. pp. IV-4-1–IV-4-8.

Rydholm, S.A. Pulping Processes, Ch. 6, General Principles of Pulping. Interscience Publishers, New York (NY), USA, 1965. pp. 277–367.

Ryti, N. Puunjalostustalous. Otakustantamo, Helsinki, Finland, 1987. 119 pp.

Seth, R. S. (1990) Fibre quality factors in papermaking - I The importance of fibre length and strength. In: Proceedings of the Materials Research Society Symposium, San Francisco (CA), USA. pp. 125–141.

Seth, R.S., Page, D.H. (1988) Fibre properties and tearing resistance. Tappi J. 71(2): 103–107.

Siau, J.F. Wood: Influence of moisture on physical properties. Department of Wood Science and Forest Products, Virginia Polytechnic Institute and State University, Blacksburg (VA), USA, 1995. 227 pp.

Silverstein, R.M., Bassler, G.C., Morrill, T.C. Spectrometric Identification of Organic Compounds, John Wiley & Sons, Inc., New York (NY), USA, 1991. 419 pp.

Song, H., Lee, S.Y. (2006) Production of succinic acid by bacterial fermentation. Enzyme Microb. Technol. 39(3): 352–361.

Srinivas, V., Rodley, G.A., Ravikumar, K., Robinson, W.T., Turnbull, M.M., Balasubramanian, D. (1997) Molecular Organization in Hydrotrope Assemblies. Langmuir 13(12): 3235–3239.

Stone, J.E. (1957) The effective capillary cross-sectional area of wood as a function of pH. Tappi J. 40(7): 539–541.

Stone, J.E., Förderreuther, C. (1956) Studies of Penetration and Diffusion into Wood. Tappi 39(10): 679–683.

Sundberg, A., Sundberg, K., Lillandt, C., Holmbom, B. (1996) Determination of hemicelluloses and pectins in wood and pulp fibres by methanolysis and gas chromatography. Nord. Pulp Pap. Res. J. 11(4): 216–219, 226.

Surewicz, W. (1974) Die Verarbeitung von Sägespänen zu gebleichten Sulfat-Papierzellstoffen. Zellst. Pap. 23(7): 196–203.

Svedman, M., Tikka, P., Luhtanen, M. (1998) Effects of softwood morphology and chip thickness on pulping with a displacement kraft batch process. Tappi J. 81(7): 157–168.

Taherzadeh, M.J., Keikhosro, K. (2007) Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review. BioRes. 2(3): 472–499.

Taylor, T.G. (1977) The production of bleached kraft market pulp from sawdust. Pulp Pap. Can. 78(1): T14–T18.

Traynard, A.R. (1955) Hydrotropic Pulping of a Tropical Wood. Tappi 38(9): 149A–150A.

Traynard, Ph., Eymery, A. (1955) Delignification des Vegetaux par les Solutions hydrotropiques, I - Mecanisme dela delignification. Holzforschung 9(6): 172–177.

Tveit, T.-M., Aaltola, J., Laukkanen, T., Laihanen, M., Fogelholm, C.-J. (2006) A framework for local and regional energy system integration between industry and municipalities—Case study UPM-Kymmene Kaukas. Energy 31(12): 2162–2175.

Uhmeier, A. (1997) Pressure-Impregnation Technique for Wood Chips. J. Pulp Pap. Sci. 23(4): J161–J167.

UNEP Hydrotropes - SIDS Initial Assessment Report For SIAM 21. United Nations Environment Programme Publications, Washington (DC), USA, 2005. 349 pp.

Usta, I. (2005) A review of the configuration of bordered pits to stimulate the fluid flow. Maderas, Cienc. tecnol. 7(2): 121–132.

Uusvaara, O. (1975) Teollisuudessa käytettävän sahanpurun ominaisuudet. Publications of the Finnish forest research institute 83. pp. 1–43.

Varade, D., Bahadur, P. (2004) Effect of Hydrotropes on an Aqueous Solution Behaviour of Surfactants. J. Surfact. Deterg. 7(3): 257–261.

Varhimo, A., Kojola, S., Penttilä, T., Laiho, R. (2003) Quality and Yield of Pulpwood in Drained Peatland Forests: Pulpwood Properties of Scots Pine in Stands of First Commercial Thinnings. Silva Fenn. 37(3): 343–357.

Virkola, N.-E. (1980) Some Results of Mill Trials with AQ as a Pulping Additive in Finland. In: Proceedings of the TAPPI 1980 Pulping Conference, pp. 479–481.

Virkola, N.-E. (1981) Would anthraquinone be economical in your pulp mill? Tappi 64(6): 51–53.

Virkola, N.-E., Pikka, O., Keitaanniemi, O. (1983) Sulfaattisellun valmistus. In: Puumassan valmistus, Suomen Paperi-insinöörien Yhdistyksen oppi- ja käsikirja II, Osa 1. Ed. Virkola, N.-E. Teknillisten tieteiden akatemia, Helsinki, Finland. pp. 291–410.

Vuorinen, T. (1993) The role of carbohydrates in alkali anthraquinone pulping. J Wood Chem. Technol. 13(1): 97–125.

Werpy, T., Petersen, G., Aden, A., Bozell, J., Holladay, J., White, J., Manheim, A., Eliot, D., Lasure, L., Jones, S. Top Value Added Chemicals from Biomass-Volume I: Results of Screening for Potential

Candidates from Sugars and Synthesis Gas. U.S. Department of Energy, Oak Ridge (TN), USA, 2004. 76 pp.

Wiedenhoeft, A.C., Miller, R.B. (2005) Structure and Function of Wood. In: Handbook of wood chemistry and wood composites. Ed. Rowell, M.R. CRC Press, Boca Raton (FL), USA. pp. 9–33.

Wilder, H.D., Daleski, E.J., Jr. (1965) Delignification Rate Studies. Part II of a Series on Kraft Pulping Kinetics. Tappi 48(5): 293–297.

Willför, S., Hemming, S., Reunanen, M., Eckerman, C., Holmbom, B. (2003) Lignans and Lipophilic Extractives in Norway Spruce Knots and Stemwood. Holzforschung 57(1): 27–36.

Willke, T., Vorlop, K.-D. (2004) Industrial bioconversion of renewable resources as an alternative to conventional chemistry. Appl. Microbiol. Biotechnol. 66(2): 131–142.

Wilson, K. (1968) Bestämning av effektivt alkali i svartlut. Sven. Papperstidn. 71(11): 446–447.

Woods, N.I. (1956) Determination of Penetration Rates of Liquid Media into Wood Using a Quartz Spiral Balance. Part II. Water and a Pre-Treatment Spruce Chip. Pulp Pap. Mag. Can. 57(5): 142–151.

Xu, Z.P., Braterman, P.S. (2003) High affinity of dodecylbenzene sulfonate for layered double hydroxide and resulting morphological changes. J. Mater. Chem. 13(2): 268–273.

Yasuda, S., Fukushima, K., Kakehi, A. (2001) Formation and chemical structures of acid-soluble lignin I: sulfuric acid treatment time and acid-soluble lignin content of hardwood. J. Wood. Sci. 47(1): 69–72.

Ylitalo, E. Puun energiakäyttö 2006. Finnish Forest Research Institute, Forest Statistical Bulletins, Helsinki, Finland, 2007. 10 pp.

Yu, Y. The effect of fiber raw material on some toughness properties of paper, Doctoral thesis, Helsinki University of Technology, Espoo, Finland, 2001. 35 pp.

Zeikus, J.G., Jain, M.K., Elankovan, P. (1999) Biotechnology of succinic acid production and markets for derived industrial products. Appl. Microbiol. Biotechnol. 51(5): 545–552.

Zobel, B.J., Sprague, J. R. Juvenile Wood in Forest Trees. Springer-Verlag, Berlin, Germany, 1998. 300 pp.

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

FCT

ÅBO AKADEMI

epnoe

European Polysaccharide
Network Of Excellence

PaPSaT

Åbo Akademi