Department of Forest Products Technology

A larch biorefinery producing pulp and lactic acid

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Abstract

In a forest based biorefinery pulp and paper are the main products, while side-streams are utilized for value-added products. Hemicelluloses can be removed from wood by extraction prior to pulping and converted into biofuels or chemicals. In this thesis a proof of concept for a process utilizing larch for production of papermaking pulp and biochemically obtained lactic acid was determined. Larch is a softwood species, which has a high content of water-soluble arabinogalactan. Therefore, water extraction suits especially larch wood. By removing the water-soluble carbohydrates with pre-extraction (PE) prior pulping, an additional sugar stream is formed.

In this study wood chips of Siberian larch (*Larix sibirica* Lebed.) were pre-extracted with water prior pulping. The optimal PE conditions were determined. Both the sugar-rich extract and the pre-extracted wood chips were analyzed in detail. PE at 150 °C for 90 min dissolved about 11% sugars on wood. A mild wash was needed to wash out the dissolved carbohydrates from the wood chips. The pre-extracted and washed wood chips were used for pulping, while the extract was fermented into lactic acid. Polysulfide (PS) and anthraquinone (AQ) were used as pulping additives to compensate for the yield loss caused by the PE. Without PS and AQ addition the pulp yield loss after PE was 5% relative to conventional kraft pulp. At a PS charge of 2% and 0.1% AQ on wood the pulp yield loss was reduced to 2%. PE allows less alkali and lower H-factor. The larch pulp was then bleached, and paper sheets were made. The unbleached PE-PSAQ larch pulp had lower tear strength and optical properties compared to kraft larch pulp. The PE-PSAQ pulp was easier to bleach, and therefore reached higher brightness. The bleached PE-PSAQ pulp had lower sheet density, poorer tensile strength, better tear strength, higher opacity, higher light scattering, and higher air permeability. PE-PSAQ pulps could be used in similar applications as other softwoods. The hydrolyzed extract was fermented with different bacteria strains. Fermentation with *Bacillus coagulans* MXL-9 gave the most attractive results. Larch extract containing 36 g/L sugars was fermented into 28 g/L lactic acid. The lactic acid yield for 97 h cultivation time was 78.5% on initial sugar and 5.8% on wood.

A process flowchart for a larch biorefinery was constructed, mass and energy balances were obtained through simulation, and the process was economically evaluated. An existing kraft pulp mill could relatively easy be converted into a larch biorefinery. The cash flow analysis showed that an additional lactic acid production for a kraft pulp mill would be profitable. The investment costs could be paid back within 16 months, when the lactic acid production was added to an existing kraft pulp mill.

Keywords biorefinery, larch, Larix sibirica, pre-extraction, fermentation, lactic acid

Sammandrag

  I ett skogsbaserat bioraffinaderi utgörs huvudprodukterna av massa och papper, medan sido-strömmarna utnyttjas till produkter med högre förädlingsvärde. Hemicellulosa kan avlägsnas från träflisen genom extraktion före massatillverkning och att därefter omvandlas till biobränsle eller kemikalier. I den här avhandlingen presenteras en process där siberisk lärk används till produktion av pappersmassa och där en biprodukt är biokemiskt framställd mjölksyra. Lärk är ett barrträd med högt innehåll av vattenlösligt arabinogalaktan. Därför lämpar sig extraktion med vatten speciellt för lärk. Genom att avlägsna de vattenlösliga kolhydraterna med förextraktion (PE) före massakok, formas ett extra sockerflöde.

  I den här studien användes träflis av sibirisk lärk (*Larix sibirica* Lebed.). Flisen extraherades med vatten före sulfatkoket. De ideala förhållandena för extraktionen bestämdes. Både det sockerrika extraktet och de extraherade träflisen analyserades detaljerat. Extraktion vid 150 °C under 90 minuter upplöser socker motsvarande 11% av veden. En mild tvätt var nödvändig för att avlägsna de upplösta kolhydraterna från träflisen. De extraherade och tvättade träflisen användes i sulfatkok, medan extraktet fermenterades till mjölksyra. Polysulfid (PS) och antra-kinon (AQ) användes som tillsatsämnen i det efterföljande sulfatkoket, för att kompensera det lägre massautbytet förorsakat av förextraktionen. Utan tillsats av PS och AQ var utbytet efter extraktion 5% lägre jämfört med ett traditionellt sulfatkok. Med PS- och AQ-doserna 2% res-pektive 0,1% av veden minskades utbytets bortfall till 2%. Förextraktionen tillåter mindre mängder alkali och lägre H-faktor. Lärkmassan blektes och pappersark framställdes. Den oblekta PE-PSAQ-lärkmassan hade något lägre rivstyrka och sämre optiska egenskaper jämfört med sulfatmassa. PE-PSAQ-massan var enklare att bleka och därför uppnåddes högre ljushet. Den blekta PE-PSAQ-massan hade lägre arkdensitet, sämre dragstyrka, bättre rivstyrka, högre opacitet, högre ljusspridning och högre permeabilitet. PE-PSAQ-lärkmassan kunde ha motsva-rande användingsmöjligheter som sulfatmassor av andra barrträd. Det hydrolyserade extraktet fermenterades med olika bakteriestammar. Fermentering med *Bacillus coagulans* MXL-9 gav de mest attraktiva resultaten. Extrakt innehållande 36 g/l socker fermenterades till 28 g/l mjölksyra. Mjölksyreutbytet för en fermenteringstid på 97 h var 78,5% av ursprungligt socker.

  Ett flödesschema för bioraffinaderiet konstruerades, mass- och energibalanser erhölls via simulering, och processen evaluerades ekonomiskt. En befintlig massafabrik kunde relativt enkelt omvandlas till ett lärkbioraffinaderi. Kassaflödet visade att en extra mjölksyre-produktion vid en massafabrik skulle vara lönsam. Investeringskostnaderna kunde betalas tillbaka inom 16 månader, ifall mjölksyreproduktionen lades till en befintlig massafabrik.

PREFACE

LIST OF PUBLICATIONS

Paper I Kämppi, R., Hörhammer, H., Leponiemi, A., and van Heiningen, A. (2010): Pre-extraction and PSAQ pulping of Siberian larch. *Nordic Pulp and Paper Research Journal* 25(2), 243-248. DOI 10.3183/NPPRJ-2010-25-02-p243-248

Paper II Hörhammer, H., Walton, S., and van Heiningen, A. (2011): A larch based biorefinery: Pre-extraction and extract fermentation to lactic acid. *Holzforschung* 65(4), 491-496. DOI 10.1515/HF.2011.085

Paper III Hörhammer, H., and van Heiningen, A. (2012): A larch biorefinery: Influence of washing and PS charge on pre-extraction PSAQ pulping. *BioResources* 7(3), 3539-3554.

Paper IV Hörhammer, H., Berezina, O., Hiltunen, E., Granström, T., and van Heiningen, A. (2012): Semi-bleached paper and fermentation products from a larch biorefinery. *Tappi Journal* 11(10), 31-39.

Paper V Hörhammer, H., Treasure, T., Gonzalez, R., and van Heiningen, A. (2014): Larch biorefinery: Technical and economic evaluation. *Industrial & Engineering Chemistry Research* 53, 1206-1213. DOI 10.1021/ ie403653j

Author's contribution

I Hanna Hörhammer carried out a part of the experiments, planned the rest of the experiments and wrote the manuscript as an equal author with Riikka Kämppi.

II, IV Hanna Hörhammer carried out most of the experiments and wrote the manuscript.

III Hanna Hörhammer carried out the experiments and wrote the manuscript.

V Hanna Hörhammer delivered the data for the simulation, made the economic evaluation and wrote the manuscript.

LIST OF SYMBOLS AND ABBREVIATIONS

IFBR	Integrated forest biorefinery
PE	Pre-extraction
LA, PLA	Lactic acid, Poly(lactic acid)
PS	Polysulfide
AQ	Anthraquinone
o.d.	Oven dried
L/W	Liquor to wood ratio
SR	Schopper Riegler
AH	Acid hydrolysis
SSF	Simultaneous enzymatic hydrolysis and fermentation
HLE	Hydrolyzed larch extract
NREL	National Renewable Energy Laboratory
GC	Gas chromatography
HPLC	High-performance liquid chromatography
HPAEC	High-performance anion-exchange chromatography
HMF	Hydroxymethylfurfural
DS	Dry solids
TOC	Total organic carbon

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1 INTRODUCTION AND OUTLINE

The traditional pulp and paper industry faces big challenges in the current market, especially in the northern part of the globe. With limited oil supply, increasing concern about greenhouse gas emissions and decreasing competiveness of pulp and paper production in temperate climates, relevant changes have to take place. Tropical wood species grow faster compared to wood species in the temperate zone. The supply of raw-material is therefore better, and the processes can be larger in capacity and more efficient in the tropical areas of the world. In order to survive and stay profitable the production in the temperate zones has to become more efficient and the usage of the raw-material has to be increased.

The biorefinery concept could be the solution for the problem and make the future brighter for the forest industry - either in the form of an independent wood biorefinery or integrated with a pulp mill. The latter concept has been described as the integrated forest biorefinery (IFBR) (van Heiningen 2006) whereby a pulp mill focuses on the possibility of producing other products in addition to or even replacing paper and board. One of these possibilities is to remove of part of the wood prior to kraft pulping and then use the extracted wood material for production of value-added products. For example, pre-extraction or pre-hydrolysis with water or an acidic aqueous solution at elevated temperatures is suited for removing hemicelluloses from wood prior to pulping. The extracted hemicelluloses are then the feedstock for new commodity products and the extracted wood is used for pulping.

There are large resources of larch in Russia, mainly Siberian larch, but also other subspecies of larch. About 38% of the 2.7 billion acres of the Russian boreal forest is Siberian larch (Nevalainen, Hosia 1969a) and there is an interest in utilizing larch for the production of pulp and paper. Larch has more water soluble components compared to other wood species, and is therefore very interesting as feedstock in the biorefinery concept. In a larch wood biorefinery water soluble carbohydrates, mainly arabinogalactan could be removed from the wood chips by a hot water treatment, also called pre-extraction or pre-hydrolysis. The extracted wood chips could go after a washing stage to pulping and ultimately be used for

papermaking. Paper made from larch kraft pulps has high tear strength, but other strength properties are somewhat weaker than pine and spruce (Hakkila et al. 1972; Einspahr et al. 1983; Uprichard, Gray 1973). However, the easier utilization of arabinogalactan as by-product could be an advantage. The sugars in the pre-extract could be fermented and converted to biofuels and lactic acid, or used for various dietary or pharmaceutical applications. Lactic acid can be converted into poly(lactic acid) (PLA), which is a biodegradable plastic. PLA has good properties i.e. good mechanical properties, thermal stability, processability and low environmental impact, and could replace plastic derived from fossil raw-material (Gruber 2006).

The objective of this research project was to investigate the pre-extraction (PE) of hemicelluloses from Siberian larch aiming at the production of a new feedstock stream for additional products as well as maintaining the production of pulp fibers at high yield and quality.

The questions which we wanted address with the present research are:

1. What is the potential for pre-extraction pulping of larch wood?

2. Which are the ideal extraction and pulping conditions?

3. What is the mechanism of hemicellulose dissolution during extraction?

4. How could the process be optimized and performed in practice?

5. What are the qualities of the products?

6. What are the economic aspects for this process concept?

The project started in March 2007. Most of the experiments were performed by Hanna Hörhammer at the Department of Forest Products Technology at Aalto University (Espoo, Finland). Riikka Kämppi did within her Master's thesis at the same department some of the pulping trials presented in this research project. The fermentation experiments with *Bacilllus coagulans* MXL-9 were carried out at Maine University (Orono, USA) by Sara Walton. The other bacteria strains were tested by Oksana Berezina at the State Research Institute of Genetics and Selection of Industrial Microorganisms in Moscow (Russia). Eero Hiltunen at our department has given valuable advice regarding paper properties. The simulation

for the process evaluation was performed at North Carolina State University (Raleigh, USA) by Trevor Treasure.

Paper I gives proof of concept for a biorefinery based on Siberian larch (*Larix sibirica* Lebed.) using pre-extraction (PE) polysulfide-anthraquinone (PSAQ) pulping. Pre-extraction of larch chips was followed by pulping with PS and AQ. The synergism of PS and AQ was beneficial for the pulp yield of the pre-extracted larch chips. Water extraction before pulping resulted in lower pulp yield than control kraft pulps. However, with addition of PS and AQ the yield loss was mostly compensated. The composition of larch wood was also presented in this paper. A preliminary techno-economic analysis of a process based on Siberian larch for production of papermaking pulp and lactic acid was included in this paper (Hörhammer et al. 2009).

The influence of extraction temperature (100-160 °C) and time on extract composition and pulp yield is presented in **Paper II**, as well as some fermentation results. The composition of both the wood residues and water extracts was determined. This gave a detailed mass balance for the pre-extraction at different conditions. Two different hydrolysis methods (acidic hydrolysis and simultaneous enzymatic hydrolysis) were tested before fermentation with *Bacillus coagulans* MXL-9 of two different extracts (36 g/L sugars and 28 g/L sugars). Based on the findings in Paper II the optimal pre-extraction conditions for this kind of a larch biorefinery was determined to water extraction at 150 °C for 90 min. The fermentation of the water extract to lactic acid proved to be attractive. The lactic acid yield for the fermentation of the extract of 36 g/L sugars approached 80%.

Paper III focuses on the effect of the degree of washing of extracted chips and the PS charge in the PSAQ pulping on the PE-PSAQ pulp yield and properties were studied. About 3/5 of the dissolved hemicellulose sugars are obtained by draining the extract after hot water treatment at L/W of 3.5 L/kg. However, because the residual dissolved sugars in the wet wood likely consume a significant amount of alkali during pulping, washing is needed between the pre-extraction and pulping step. Three different levels of washing (no, mild and extensive) and three different PS charges (0.5, 1.0, and 2.0%) were tested. These PS charges are more practically viable than 4% used in paper I and II. The characteristics of the extract, wash water, pulp, and black liquor samples were also determined. The dry matter, ash content and heating value of the black liquor were determined in order to quantify the effect of the extraction on its combustion properties. A mild

wash of the extracted chips before the cooking stage is sufficient to remove most of the dissolved carbohydrates, while a PS charge of 2.0% significantly compensates for the yield loss due to the pre-extraction.

In **Paper IV** the products produced from a larch biorefinery are studied. The PE-PSAQ pulps were bleached and laboratory paper sheets were produced and tested. The larch water extract was fermented into different fermentation products i.e. acetate, lactate, ethanol, butanol and butyrate, using several different bacteria strains. The removal of hemicelluloses through pre-extraction results in somewhat more porous paper, but generally the paper properties are comparable to other industrial softwood kraft pulps. The bacteria strains tested in **Paper IV** did not give better results than the trials with *Bacillus coagulans* MXL-9.

Finally, the entire larch biorefinery process was simulated in detail in order to evaluate the process technically and economically. The results from the process evaluation are presented in **Paper V**. Two different larch biorefinery processes (PS charge 0.5% and 2.0%) were compared to a conventional larch kraft process. A process scheme based on practical solutions and containing equipment available on the market was adopted for techno-economic study. Besides the units traditionally present in a conventional kraft process, the following additional units are needed for the larch biorefinery: extraction of wood chips, hydrolysis and neutralization of extract, fermentation, purification of lactic acid, and a MOXY reactor for the preparation of the PS liquor. Variable and fixed costs were estimated, and the cash flows determined for the three different cases. According to the results the larch biorefinery process would be capable of rather quickly pay back the required investment costs.

2 LITERATURE OVERVIEW

2.1 The integrated forest biorefinery (IFBR)

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass (NREL 2012). The idea is to efficiently use the biomass raw-material and convert it into biomaterials or biofuels. In a forest biorefinery wood or forest biomass is converted to different products. The wood is subjected to fractionation and conversion processes. The fractionation process results in wood components for further processing, whereas conversion of these components results in usable products i.e. chemicals and other products. The following chemicals could be extracted from wood: tannins, colorants, medical compounds, bark extracts for pharmaceutical use and water-soluble polysaccharides. There are certain challenges for wood biorefineries. It is difficult to find usage for all parts from the tree. The chemical and physical differences between softwood and hardwood species and the complex composition of wood make the operating of a wood biorefinery more challenging. Additionally, there are other competing raw-materials on the market. The potential for wood biorefineries is very limited in the near future, but more success may be achieved by integration of the biorefinery concept in a pulp mill. (Niemelä 2009)

A chemical pulp mill could be transformed into an integrated forest biorefinery (IFBR) (van Heiningen 2006). Besides the production of pulp different co-products could be produced. Co-products such as transportation fuels, polymers and other chemicals could be utilized from the side or waste streams. In other words, pulp would remain the core product and be produced mainly of cellulose. Chemicals and polymers could be produced from hemicelluloses, and transportation fuel could be made out from black liquor. The bark and other biomass could be used as fuel for the pulp mill. Simultaneously, the impact on the environment would decrease. Chemicals could be produced in an IFBR from the following steps: pre-extraction of wood chips before pulping, separation of components from black liquor after pulping, processing of black liquor and processing of sludge from waste water treatment. (Niemelä 2009)

In conventional kraft pulping processes most of the hemicelluloses are dissolved in the black liquor and then subsequently combusted. Since the hemicelluloses have a relatively low heating value, the combustion represents uneconomical use of the feedstock resource. In an IFBR the wood chips are treated before pulping in order to remove hemicelluloses. The hemicelluloses are extracted from the wood with water or a caustic solution at temperatures above 100 °C. This will produce a stream with dissolved hemicelluloses, which can be further utilized for value-added products. The extracted wood chips will then be used in the pulping process. Besides generating a feed stream for new bioproducts, the pre-extraction also results in several benefits regarding the pulping process i.e. decreased alkali consumption, increased delignification rate and reduced black liquor load. (van Heiningen 2006; Huang et al. 2008)

A variety of effective pretreatment methods to remove or hydrolyze the hemicelluloses from the wood prior to pulping have been investigated. The following methods work efficiently on wood hemicelluloses: dilute acid pretreatment, liquid hot water extraction, steam explosion-based extraction, dilute acid-steam explosion and alkaline extraction. Ammonia fiber/freeze explosion (AFEX) does not seem to remove hemicelluloses efficiently, although it works well on lignin. (Huang et al. 2008)

The stream containing hemicelluloses is subjected to a series of conversion and separation processes in order to produce ethanol, sugar based polymers and chemicals. Black liquor containing dissolved lignin can be further gasified to produce syngas. The resulting syngas can be further converted into methanol, dimethyl ether, higher alcohols, acetic acid, Fisher-Tropsch chemicals, electricity and process steam. According to the description above, the IFBR can make full use of all the feedstock components to produce multiple value-added co-products including energy and various chemicals, along with the major products such as paper and electricity. (van Heiningen 2006; Huang et al. 2008)

Black liquors could be utilized more efficiently in the future. Today most of the black liquors are combusted, but some compounds are, however, already separated from them before combustion: turpentine, tall oil and lignin. In the future there is good potential also for acetic and formic acid, hydroxy acids (glucoisosaccharinic, xyloisosaccharinic, 2,5-dihydroxybutanoic, lactic and glycolic), polysaccharides and volatile compounds such as methanol. (Niemelä 2009)

Many different existing and new products could be obtained from an IFBR. Wood, pulp and paper products would remain as important products. Also different forms of energy i.e. heat and electricity could be taken out from the process. The IFBR makes it possible to simultaneously produce transportation fuels like ethanol, methanol, other alcohols, dimethyl ether (DME) biodiesel and biogas (Niemelä 2009). There is a big potential for producing different polymers and other chemicals from an IFBR. The following sugar-derived chemicals could be produced: 1,4-diacids (succinic, fumaric, malic), 2,5-furandicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolacetone, glycerol, sorbitol and xylitol (Cullinan 2006).

By integrating the biorefinery concept an existing mill has the opportunity to generate significant amounts of bioenergy and bioproducts to significantly increase its revenue, while continuing to produce wood, pulp and paper products. For forestry companies that would like to apply the IFBR concept it is difficult to decide which biorefinery products to produce, because of the large variety of products and the effect on the company's economic success. Besides choosing the optimal product portfolio and right processes (biochemical, thermochemical or chemical) for the new IFBR, there are also several other questions to be answered. Which would be the best business partners and business models for implementing the IFBR? And how could the targeted return on investment be achieved? (Chambost 2008)

Adapting the biorefinery concept would be a very logical development for the forest industry. The raw-material (biomass) and the infrastructure for handling and knowledge of biomass already exist. The pulp and paper industry is in a unique situation, because the IFBR would increase energy efficiency and reduce CO_2 emissions. With help of the IFBR more raw-material would be converted into products and therefore the potential for increased profitability and efficiency of the mill would increase. (Couch 2006)

There are still barriers for the IFBR concept, before a real breakthrough can take place (van Heiningen 2010). The two main barriers are; high transport costs of solid biomass, and lack of cost effective fractionation and conversion technologies for lignocellulosic biomass. Many research teams are trying to develop processes for biomass, but at the moment the available processes are not efficient enough. Fractionation and conversion technologies for hemicelluloses, lignin and cellulose

must be further developed. The oil price is still too low for making the production of transportation fuels from woody biomass profitable.

Considering these barriers the focus of the IFBR should be on both high value-added products i.e. specialty chemicals and nutraceuticals, and bulk chemicals i.e. kraft lignin and commodity polymers. The product portfolio and process technology would be chosen case by case depending on the raw material. Through different routes a wide variety of products could be produced in addition to paper products. The production would the more efficient and the revenue could be increased. The biorefinery concept could be the solution for the traditional paper industry in the temperate zone, which is currently facing big challenges in the market and must find new ways to remain competitive.

In one of these forest biorefinery concepts the hemicelluloses are extracted before kraft pulping, and then they are utilized as feedstock for biofuels or biochemicals production, while the extracted wood chips are pulped into kraft fibers (Frederick et al. 2008; Yoon, van Heiningen 2008; Al-Dajani et al. 2009; Amidon, Liu 2009; Helmerius et al. 2010; **Paper I**; Vila et al. 2011; Yoon et al. 2011). The hemicelluloses have been used for the production of liquid fuels such as ethanol (Walton et al. 2010; Liu et al. 2010), butanol (Survase et al. 2011), jet and diesel fuel (Xing et al. 2010), and gasoline (Li et al. 2011). Chemical conversion of hemicelluloses into commodity chemicals such as furfural, formic, and acetic acid has been reported by Xing et al. (Xing et al. 2011), and their fermentation into lactic acid by Walton et al. (Walton et al. 2010).

2.2 Characteristics of larch

2.2.1   General characteristics and subspecies

Larch trees are conifers and rather tolerant to harsh growing conditions (Hakkila et al. 1972). They grow in the cooler temperate northern hemisphere, and often form the tree limit going north and up the mountains. The characteristics of larch depend on the growing conditions. Although larch is a conifer, larches lose their needle-like leaves every autumn. The needles turn yellow and fall to the ground, which leaves the larch tree leaf-free during the winter. The cones of larch trees are small and round or oval. The trunks of older larches are generally very straight, and the wood is durable and rot resistant. The larch root system is strong and deep i.e. similar to that of pine. (Reinikainen 1997)

There are several subspecies of larch, and these subspecies have their specific growing areas. There are certain differences between different subspecies of larch, at least in the appearance of the leaves and cones. Globally, the most common and largest larch resources consist of Siberian larch, Dahurian larch and Tamarack larch. Siberian larch (*Larix sibirica* Lebed.) grows in the western and central parts of Russia, whereas the growing area of Dahurian larch (*Larix gmelinii* (Rupr.) Rupr.) is in the eastern parts of Russia. The Tamarack larch (*Larix laricina* (Du Roi) K. Koch) grows in Canada. In the Alp region of Europe there are some small areas with European larch (*Larix decidua* Mill.), and smaller quantities of Japanese larch (*Larix kaempferi* (Lamb.) Carrière) grow in Japan. There are also some additional larch subspecies in certain parts of China and in western Canada. (Juvonen 1986; Reinikainen 1997)

2.2.2   Composition and structure

The chemical composition of larch differs slightly from other softwood species i.e. pine and spruce. Larch wood has a large amount of heartwood, up to 80%, and is denser than other softwood species (Nevalainen, Hosia 1969a). Larch has higher content of water-soluble arabinogalactan (Nevalainen, Hosia 1969a; Sjöström 1993; Alén 2000; Shimizu 2001). The content of arabinogalactan in larch heartwood can be up to 30%, whereas it is less than 1% in other softwood species (Nevalainen, Hosia 1969a). **Table 1** presents the chemical composition of spruce, pine and larch (Nevalainen, Hosia 1969a).

Table 1 Carbohydrate composition as % of carbohydrates of spruce, pine and larch (Nevalainen, Hosia 1969a).

Wood species	Galactan	Glucan	Mannan	Arabinose	Xylan
Spruce	6.0	65.5	16.0	3.5	9.0
Pine	6.0	65.0	12.5	3.5	13.0
Larch	17.5	63.0	7.5	3.0	9.0

Larch wood arabinogalactan has a backbone of β-(1→3)-linked D-galactopyranose units and is highly branched at C_6 (Alén 2000). The side chains are composed of β-(1→6)-linked D-galactose units, D-galactose and L-arabinose units or single L-arabinose units and single D-glucuronic acid units (**Figure 1**). The arabinogalactan in larch wood is located in the lumen of the cell, whereas the galactoglucomannan in spruce wood is a

structural component in the secondary wall (Côté et al. 1966; Willför et al. 2002). The lignin content of larch wood is similar to that of spruce and pine, while pine has somewhat more extractives than spruce and larch (Nevalainen, Hosia 1969a). The major difference between the chemical composition of larch, spruce, and pine is the presence of arabinogalactan and taxifolin in larch wood. The heartwood of larch contains flavonoids, which make larch wood resistant against microorganisms. Larch wood can therefore be used for certain building constructions without the use of preservatives.
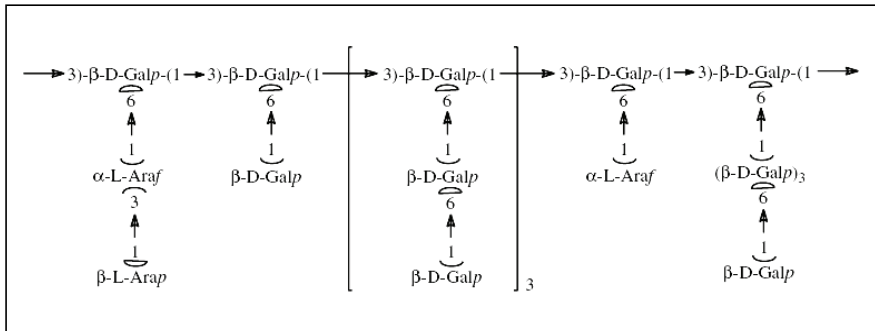
Figure 1 Arabinogalactan in larch wood (Alén 2000).

Larch has a higher basic density than pine and spruce. The basic density of Siberian larch is between 450 and 500 kg/m³, while for pine it is between 350 and 450 kg/m³ and for spruce around 400 kg/m³. There are also differences between different larch species. Here are the basic densities of 50-year-old larch trees; Siberian larch 491 kg/m³, European larch 476 kg/m³, Japanese larch 440 kg/m³, and Dahurian larch 522 kg/m³. The bark content is also slightly higher for Siberian larch wood (12-20%) than for pine (5-15%) and spruce (8-12%). (Hakkila et al. 1972)

Like other softwoods, larch wood is composed mainly of longitudinal tracheids and ray parenchyma cells. The morphology is very similar to that of spruce. The greatest difference between the fibers in larch and pine is the absence of longitudinal parenchyma cells in pine. Based on morphology different larch subspecies cannot be distinguished. Tracheids take up about 90% of the wood volume by larch, while about 10% consists of ray cells. In larch wood there are normal longitudinal tracheids, longitudinal parenchyma cells and strand tracheids. The strand tracheids are short longitudinal tracheids. Strand tracheids

and longitudinal parenchyma cells differ from each other in cell wall thickness and type of pits. The cell wall in strand tracheids is greater. The pits are bordered in strand tracheids and simple in longitudinal parenchyma cells. In addition to the different types of cells, larch wood contains resin canals, which are tube-like intercellular spaces present both in vertical and horizontal directions. (Juvonen 1986)

2.2.3   Pulping and papermaking of larch

Generally, larch kraft pulp has lower yield than kraft pulp of pine or spruce (Einspahr et al. 1983; Isebrands et al. 1982; Bobrow 1974; Uprichard, Gray 1973; Hakkila et al. 1972; Nevalainen, Hosia 1969b). The high amount of water-soluble arabinogalactan in larch wood results in higher consumption of cooking chemicals, and also poorer pulping yield than for other softwoods (Nevalainen, Hosia 1969b; Hakkila et al. 1972). The viscosity of unbleached kraft pulp is higher for larch than for other softwood species (Nevalainen, Hosia 1969b; Hakkila et al. 1972).

The brightness of unbleached kraft pulp is lower for larch than for pine and spruce (Nevalainen, Hosia 1969b). The bleachability of larch pulp seems to be good, because after CEHDED (C = chlorine, E = alkaline extraction, H = hypochlorite, D = chlorine dioxide) bleaching the final brightness of Siberian larch kraft pulp and Scots pine kraft pulp were equal (Hakkila et al. 1972). However, the brightness reversion of bleached larch pulp is greater compared to that of pine pulp, presumably due to higher content of extractives soluble in methylene chloride. Yield losses during bleaching are similar between larch and pine pulps. The sheet density of larch is lower compared to Scots pine and Norway spruce (Nevalainen, Hosia 1969b). The tensile and bursting strengths of larch are notably lower than those of pine and spruce pulps, whereas the tear strength of larch pulp is higher at the same level of beating (Nevalainen, Hosia 1969b). These strength properties of larch are due to its thick-walled latewood fibers.

2.3   Extraction of hemicelluloses

Pre-extraction or pre-hydrolysis using water or an acidic aqueous solution at elevated temperatures can be used to remove hemicelluloses from biomass prior to pulping. Water hydrolysis of wood was already studied in the 1940s (Overbeck,

Muller 1942). During water extraction the acetyl groups of the hemicellulose are released as acetic acid, leading to a decrease in pH of the extract. The increased acidity leads to cleavage of glycosidic bonds and thus reduced molecular weight of the hemicelluloses so that they become soluble (Chen et al. 2010; Song et al. 2008). Hot-water extraction is therefore autocatalytic and is called autohydrolysis (Amidon, Liu 2009).

During the pre-extraction carbohydrates are mainly degrading due to hydrolysis of the glycosidic bonds and the easily accessible hemicelluloses are first degraded (Leschinsky et al. 2009). The pre-hydrolysis kraft process is a well-known two-stage method to produce high-grade dissolving pulps with high cellulose content for the preparation of cellulose derivates (Sixta 2006; Bajpai, Bajpai 2001; Kerr, Harwood 1976). The high sugar content of the hydrolysate due to the high water solubility of arabinogalactans is an advantage for larch wood as a raw material for the pre-extraction process (Nevalainen, Hosia 1969b).

Unfortunately, as a result of the acidic conditions, high temperature pre-extraction with water leads to a significant pulp yield and paper strength loss after subsequent kraft pulping. For bleachable grade kraft pulp made from loblolly pine a yield loss of 6% is obtained at about 8% (both on original wood) sugars in the extract (Yoon et al. 2008; Yoon, van Heiningen 2008), similar to 7% yield loss at about 7% extract sugars for Scots pine (Kautto et al. 2010). For a bleachable grade hardwood kraft pulp the yield loss for silver birch after a mild water hydrolysis is about 4% at 4% sugars in the water extract (Helmerius et al. 2010), 10% yield loss for Eucalyptus globulus at a similar percentage of sugar extraction (Mendes et al. 2009), and about 11% pulp yield loss after collecting the same level of sugars in the water extract for aspen (Al-Dajani et al. 2009).

Similarly as the intensity of the pulping process can be described by the H-factor, the intensity of the pre-extraction is described by the pre-hydrolysis factor or P-factor (Sixta 2006). The P-factor combines the time and the temperature of the pre-extraction and can therefore be expressed as a single variable. More wood hemicelluloses are dissolved with increasing P-factor. **Equation 1** presents the definition of the P-factor. Pre-extraction at 160 °C for 60 min results in a P-factor of about 325, when using the activation energy of 125.6 kJ/mol for xylan removal.

$$P = \int_0^{t_X} \frac{k_{PX}[T(t)]}{k_{PX,REF}} dt = \int_0^{t_X} \exp\left(A' - \frac{B'}{T(t)} \right) dt \qquad \textbf{Equation 1}$$

2.4 PSAQ pulping

Polysulfide (PS) and anthraquinone (AQ) are well-known pulping additives to increase pulp yield. PS and AQ oxidize the reducing end groups of polysaccharides to aldonic acid groups, thus stabilizing the polysaccharides against peeling reactions (Teder 1969; Dimmel et al. 2003). AQ additionally accelerates the delignification rate of pulping by fragmenting and dissolving lignin (Dimmel et al. 2003). In softwood the yield is enhanced by higher retention of glucomannans due to PS and better preservation of cellulose due to AQ (Pekkala 1986). A synergism exists when PS and AQ are used together in alkaline pulping (Dimmel et al. 2003; Pekkala 1986; Luthe, Berry 2005; Jiang 1995; Berthold et al. 1999; Sturgeoff, Bernhard 1998; Li et al. 1998). The synergetic yield increase of PSAQ pulp is 0.5-1.5% (Pekkala 1986; Luthe, Berry 2005; Thompson et al. 1998; Li et al. 1998). In PSAQ pulping glucomannan is the main hemicellulose that contributes to the yield increase (Pekkala 1986; Luthe, Berry 2005; Jiang 1995). Modified pulping with polysulfide (PS) and anthraquinone (AQ) may compensate for the yield loss of kraft pulp as a result of the pre-extraction process.

2.5 Hydrolysis and fermentation of extracts

Fermentation is the action of yeasts or bacteria on carbohydrates. The hemicellulose-rich extract cannot be directly fermented into valuable commodity products. Most industrial microorganisms ferment only mono- and disaccharides, and therefore the extract has to be hydrolyzed before fermentation. The hydrolysis can be in form of acidic hydrolysis or by enzymatic hydrolysis. The choice of microorganism for producing target substances is determined by sugar composition of the hydrolysate and substrate specificity of a strain. It is also important to consider its tolerance to hydrolysis by-products, such as acetic and formic acids, furfural, HMF, and arsenate (contaminant of technical sulfuric acid) inhibiting fermentation at high concentrations. By-products are toxic to most industrial microorganisms, but the concentration of inhibitors depends on temperature and duration of the hydrolysis and the source of plant raw material (Zverlov et al. 2006). The problem is solved by detoxification of acid hydrolysates, or by searching for microorganisms tolerant to inhibitors.

2.6   Value-added products

In the traditional pulping process the hemicelluloses are burnt in the recovery boiler. Instead, the hemicelluloses could be converted into value-added products. Hemicelluloses can for example be used for the production of liquid fuels such as ethanol (Walton et al. 2010; Liu et al. 2010), butanol (Survase et al. 2011), jet and diesel fuel (Xing et al. 2010), and gasoline (Li et al. 2011). Chemical conversion of hemicelluloses into commodity chemicals such as furfural, formic, and acetic acid has been reported by Xing et al. (Xing et al. 2011), and their fermentation into lactic acid by Walton et al. (Walton et al. 2010) and Hörhammer et al. (**Paper II**).

2.7   Lactic acid and its production

Lactic acid ($C_3H_6O_3$, 2-hydroxypropionic acid) is a commodity chemical used in food, chemical and pharmaceutical applications (NNFCC 2010, Gruber et al. 2006). Lactic acid is traditionally used in the food industry, for example in the production of yoghurt. With time the application area for lactic acid has broadened and today lactic acid is also used for production of different polymer applications. Lactic acid is used as a preservative and pH-adjusting agent in food and beverages. In personal care products it is used because of its moisturising, pH-regulating and skin lightening properties. Lactic acid is the building block chemical for poly(lactic acid) (PLA), which is a biodegradable thermoplastic (NNFCC 2010; Garlotta 2001). In the future promising end-use products for lactic acid are biodegradable plastics (Global Industry Analysts 2012), which could replace the synthetic plastics.

Lactic acid can be produced through chemical synthesis or carbohydrate fermentation. Today most of the lactic acid is produced by fermentation routes (NNFCC 2010; Datta, Henry 2006; Gruber et al. 2006; Wolf et al. 2005). In order to make the sugars accessible for fermentation, the biomass is extracted and hydrolyzed. During the fermentation, microorganisms convert the carbohydrates into lactic acid. Successful lactic acid fermentation needs the right combination of microorganism, sugars, nutrients and neutralizing agents in order to economically produce lactic acid of sufficient purity.

The conventional carbohydrate fermentation process has not been economically or ecologically attractive due to high process costs and gypsum formation (Datta, Henry 2006). The separation and purification steps required complex and

expensive processes. Therefore, lactic acid has traditionally not been a large-volume chemical. Recently, the critical technologies have developed and there are now more feasible methods available for lactic acid production. The development in membrane technology has made lactic acid production possible without the formation of salt. A two-stage electrodialysis method was introduced (Glassner, Datta 1990). In the desalting step sodium lactate is recovered, purified and concentrated. In the water-splitting step lactic acid is regenerated from sodium lactate, and sodium hydroxide is recovered and purified.

Lactic acid is being produced in the United States, Western Europe and Asia-Pacific (NNFCC 2010; Datta, Henry 2006). In China the production and consumption of lactic acid will most probably increase (Global Industry Analysts 2012). Earlier there was only a limited amount of companies on the lactic acid market. The traditional lactic acid companies are Purac and NatureWorks LLC, but now there are also several Asian companies producing lactic acid. Today Purac operates production plants in the USA, The Netherlands, Spain, Brazil and Thailand (Purac 2013). NatureWorks LLC is located in Blair in the United States, and uses corn starch as raw material for lactic acid production (NatureWorks LLC 2013). The global market for lactic acid is forecast to reach about 330.000 metric tons/year by the year 2015 (Global Industry Analysts 2012). In the future a variety of biomass could be used as raw material for carbohydrate fermentation into lactic acid, for example carbohydrates from woody biomass which would not compete with food or feed.

3   MATERIALS AND METHODS

Wood chips of Siberian larch (*Larix sibirica* Lebed.) were processed in this study. The chips were pre-extracted with water prior to pulping. Polysulfide (PS) and anthraquinone (AQ) were used as pulping additives. Washing of pre-extracted chips was also investigated. The charges and conditions were optimized. Also kraft cooks were carried out as reference. The pulps were bleached, and paper sheets were made and tested. The hemicellulose-rich extracts were fermented. A larch biorefinery concept was developed. Finally, the techno-economics of the larch biorefinery producing Kraft pulp and lactic acid were determined. The methods used are listed in **Table 2**.

3.1   Wood chips

Siberian larch (*Larix sibirica* Lebed.) mill chips from the Baikal region in Russia were used. Chips were defrosted and screened to remove oversize chips and fines (SCAN-CM 40:01). The screened chips were re-frozen and stored. The dry matter of the chips was 60% (SCAN-CM 39:94), and the basic density 466 kg/m³ (SCAN-CM 43:95). Shortly before actual processing they were again defrosted. 300 g o.d. chips were used for each trial.

3.2   Pre-extraction with water

The laboratory water pre-extractions were conducted in a hot air-bath cooking system containing six rotating autoclaves (2.5 L each). For the pre-extraction (PE) the autoclaves were charged with 300 g o.d. larch wood chips and water at a liquor-to-wood ratio (L/W) of 3.5 L/kg o.d. In the first PE trials a rather high temperature of 160 °C was used in order to avoid very long PE times. In these PE trials the heat-up time was 65 min and the time at temperature was 60 min.

The operating conditions of water PE of larch wood were then more thoroughly studied. The PE trials were performed at four temperatures (100, 120, 140 and 160 °C) and five extraction times (30, 60, 90, 120 and 180 min). The heat-up time was 60 min in all PE trials and has not been included in the above mentioned extraction times. After water extraction the extract was drained. The extracted

Table 2 Experimental methods.

Analysis	Method
Screening of chips	SCAN-CM 40:01
Dry matter of chips	SCAN-CM 39:94
Density of chips	SCAN-CM 43:95
Carbohydrates in wood, pulp (hydrolysis)	NREL TP-510-42618
Carbohydrates in wood, pulp (methanolysis-GC)	Holmbom, Örså 1993
Carbohydrates in wood, pulp (hydrolysis)	Puls et al. 1985; Tenkanen, Siika-aho 2000
Carbohydrates in extract	NREL TP-510-42623
Insoluble lignin in wood, pulp	NREL TP-510-42618
Insoluble lignin in wood, pulp	KCL; 115b:82
Insoluble lignin in extract	NREL TP-510-42623
Soluble lignin (280 nm, 24.3 L/g cm)	Alén, Hartus 1988
Soluble lignin (205 nm, 110 L/g cm)	TAPPI UM 250
Extractives in wood, pulp	SCAN-CM 50:94
Acetyl groups	NREL TP-510-42618
Ash in wood, pulp	NREL TP-510-42622
Furfural, HMF	HPLC
Acetic acid, formic acid	Assay kits, Megazyme International 2010
Uronic acid groups in wood (methanolysis-GC; evaporation in rotavap equipment)	Alves et al. 2010
Nitrogen in wood	CEN/TS 15104:2005 (Nab Labs)
TOC in extract	SFS-EN 1484
Cooking liquor (effective alkali, active alkali, sulfidity)	SCAN-N 2:88
Kappa number of pulp	SCAN-C 1:00
Viscosity of pulp	SCAN-CM 15:99
Residual alkali in black liquor	SCAN-N 33:94
Dry solids of black liquor	SCAN-N 22:96
Ash in black liquor (700 °C)	KCL 59:83
Total Na in black liquor	KCL Internal (ICP)
Total S in black liquor	KCL Internal (ICP)
Heating value of black liquor	DIN 51900 (Nab Labs)
Chloride, peroxide concentration	Iodometric titration
Schopper Riegler	ISO 5267-1
Making laboratory sheets	ISO 5269
Conditioning of laboratory sheets	ISO 187
Basis weight, density, bulk	ISO 534
Roughness	SCAN-P 21:67
Air permeability	SCAN-P 60:87
ISO brightness	ISO 2470
Opacity	ISO 2471
Light scattering, absorption	ISO 9416
Tensile strength	ISO 1924-2
Tear strength	ISO 1974
Zero span (dry)	TAPPI T 279 pm-99

chips were then thoroughly washed with fresh water. The wash water was not added to the extract.

The last PE trials were conducted at 150 °C for 90 min (heat-up time of 60 min not included), which had been determined to be the optimal PE conditions for the larch biorefinery concept (**Paper II**). Otherwise, the conditions were the same as in previous PE trials. Again, the extract was drained out after the PE. The pH of the liquors was measured with a pH electrode and the density was determined by weighing a certain volume of the sample at 23 °C.

3.3 Washing of extracted chips

In the first trials, the pre-extracted chips were extensively washed with fresh water. Extensive washing includes 2 times 10 min washing in 5 L water at 23 °C followed by immersing in 25 L water overnight. Later, there were also experiments without washing and with only a mild wash of the pre-extracted chips. In the case of no washing, the extracted and drained chips were centrifuged and then led to pulping. In the mild washing procedure fresh water was added to the drained chips to again obtain a L/W ratio of 3.5 L/kg (o.d.) and then kept at 80 °C for 60 min (heat-up time of 30 min not included). The mild washing was carried out in the rotating air-bath cooking system. Before pulping the washed chips were centrifuged.

3.4 Pulping

The pulping trials were performed in the same digester as the pre-extraction trials i.e. a hot air-bath cooking system containing six rotating autoclaves (2.5 L each). The H-factor, combining temperature and time into a single variable representing the extent of the pulping (Vroom 1957), was controlled by computer. For pulping the autoclaves were charged with cooking liquor and the non-extracted or extracted wood chips. The cooking temperature was 167 °C in all cooks, and the heat-up time was 60 min. The cooking liquors, i.e. white liquor and PS liquor, were analyzed according to SCAN-N 2:88 using an automatic titrator (Mettler Toledo DL53, Switzerland) shortly before the cook.

3.4.1 Kraft pulping

Conventional kraft cooks were conducted as references for the other cooks. Mill white liquor was used as cooking liquor. The effective alkali charge of the white

liquor was 19-23%, and the sulfidity 35-37%. H-factor and effective alkali charge were varied in order to achieve pulps with different kappa numbers. The conditions for the experiments of kraft pulping are in detail presented in **Table 10**.

3.4.2 Pulping with additives

The effect of using polysulfide (PS) and anthraquinone (AQ) as pulping additives when pulping with larch wood was tested. Different PS charges were used equivalent to elemental sulfur charges of 0-4% based on o.d. wood. The PS liquor was prepared by dissolving the required amount of elemental sulfur in mill white liquor at about 70 °C and mixing constantly for 20 min. For each PS cook sodium hydroxide (NaOH) was added to compensate for the consumption of hydroxyl ions so that the concentration of NaOH was the same as that in the original mill white liquor. Fresh PS liquor was prepared for each cook. The conditions for the so called PS pulping trials are presented in **Table 11**. Some pulping trials had both polysulfide (PS) and anthraquinone (AQ) as pulping additives during the cook, i.e. PSAQ pulping. The AQ suspension was diluted to a solids content of about 8% and was added to the PS liquor when the bombs were charged for the cook. Two different AQ charges were used 0.05% and 0.1%. The conditions for the PSAQ cooks are presented in **Table 11**.

3.4.3 PE prior to pulping

Experiments on pre-extraction (PE) at 160 °C for 60 min prior to kraft, PS and PSAQ pulping were performed. The detailed process conditions for these trails are presented in **Table 12**, **Table 13** and **Table 14**.

3.4.4 PE and washing before PSAQ pulping

Most experiments included pre-extraction (PE) and washing before PSAQ pulping. The wood chips were pre-extracted at 150 °C for 90 min. After PE three different levels of washing were tested: no, mild and extensive. The PSAQ pulping was conducted under the following conditions: L/W 3.5 L/kg (o.d.), effective alkali (as NaOH) 20%, AQ 0.1%, sulfidity 38%, cooking temperature 167 °C, and H-factor 1250 h. Three different PS charges were tested; 0.5%, 1.0%, and 2.0%. Detailed pulping conditions are presented in **Table 17**.

3.4.5 Treatments after cooking

The pulps were thoroughly washed, screened using a flat screen with 0.35 mm slots, and homogenized before analyses. Pulping yields and rejects (particles retained by the screen) were determined. Kappa number (SCAN-C 1:00) and viscosity (SCAN-CM 15:99) were determined for all pulps. Residual alkali (SCAN-N 33:94) and pH were determined for all black liquor samples. The heating value of three black liquor samples was determined by Nab Labs Oy (Rauma, Finland) according to DIN 51900. The composition of pulps and black liquor samples were also studied.

3.5 Bleaching

Three pulps with kappa number around 26 were selected for bleaching trials: a kraft pulp, and two PE-PSAQ pulps with different PS charge i.e. 1) kraft, 2) PE-Mild-PS(0.5%)AQ, and 3) PE-Mild-PS(2.0%)AQ. The pulps were bleached according to the bleaching sequence O-D0-Ep-D2-P. The description and conditions for each bleaching stage are presented in **Table 3**. The oxygen delignification was conducted in the hot air-bath cooking system also used for pre-extraction and pulping. The rest of the bleaching stages were performed with plastic bags and water baths. Kappa, pH and residual chemicals were determined after most stages. The ISO brightness (ISO 2470) was determined after the D1 stage.

Table 3 Descriptions and conditions for bleaching stages.

Bleaching sequences		Concistency %	Charge %	Temperature C	Time min
O	Oxygen delignification (6 bar)	10	NaOH 2.5% Mg 0.5%	95	90
D0	Chlorine dioxide	10	ClO2 3.0% H2SO4 0.65%	60	60
EP	Alkaline extraction with hydrogen peroxide	10	NaOH 1.0% H2O2 0.9%	85	90
D1	Chlorine dioxide	10	ClO2 0.7% H2SO4 0.4%	60	60
P	Peroxide	10	NaOH 1.0% Mg 0.05% H2O2 0.8%	80	180

3.6 Pulp and paper properties

Pulp and paper properties of both unbleached and bleached pulps were studied. The unbleached pulps were beaten using a PFI mill for 1000 revolutions, before laboratory paper sheet were made. Fiber properties of the bleached and unbeaten pulp were analyzed with a FiberLab device (KajaaniFiberLab, Finland, 2003). The bleached pulps were beaten with a PFI mill for 2000 revolutions.

The beaten pulps were diluted with water to consistency of 2 g/L and the Schopper Riegler (SR) numbers were determined according to standard ISO 5267-1. Then the pulp suspensions were further diluted and laboratory paper sheets were prepared using a sheet former according to standard ISO 5269. The paper sheets were wet pressed and then dried on drying drums at 65 °C for 2 h. The laboratory paper sheets were then conditioned at certain humidity and temperature before testing (ISO 187).

The laboratory paper sheets were then tested. The following paper properties were determined for the unbleached pulps: density (ISO 534), ISO brightness (ISO 2470), tensile strength (ISO 1924-2), tear strength (ISO 1974) and zero span (TAPPI T 279 pm-99). On the bleached pulps the following paper properties were determined: basis weight, density and bulk (ISO 534), roughness (SCAN-P 21:67), air permeability (SCAN-P 60:87), ISO brightness (ISO 2470), opacity (ISO 2471), light scattering and absorption (ISO 9416), tensile strength (ISO 1924-2), tear strength (ISO 1974) and zero span (TAPPI T 279 pm-99).

3.7 Fermentation

The first fermentation experiments were performed at the University of Maine, USA, on two different kind of extracts; one produced through water extraction at 120 °C and the other at 160 °C. Two different hydrolysis methods were also tested; i.e. acid hydrolysis (AH) prior to fermentation or simultaneous enzymatic hydrolysis and fermentation (SSF). In total four fermentations were conducted; 120 °C extract/ AH, 120 °C extract/ SSF, 160 °C extract/ AH and 160 °C extract/ SSF. No duplicates were carried out. During AH the extract samples were hydrolyzed at pH 1.0 with sulfuric acid at 121 °C for 1 hour.

Enzymes used for the SSF treatment were a mixture of 4 different solutions from the Novozymes Biomass Hydrolysis kit: NS50012, NS50030, NS2202, and NS50014, as well as a Fluka xylanase derived from Trichoderma viride. For the

fermentation *Bacillus coagulans* MXL-9 was supplied by the USDA ARS (Peoria, IL, USA). Fermentation was performed in 400 mL DASGIP bio-reactors with a working volume of 250 mL (DASGIP BioTools, Shrewsbury, MA, USA). The pH was maintained at 6.5 by automatic addition of potassium hydroxide (KOH, 2 N). Vessels were sparged with nitrogen prior to inoculation and maintained at negative redox values, indicating anaerobic growth. Temperature was maintained at 50 °C and agitation at 250 RPM by magnetic stirring.

The second set of fermentation experiments were carried out at the State Research Institute of Genetics and Selection of Industrial Microorganisms in Moscow, Russia. Different bacteria strains were tested. Before fermentation the larch water extract was treated with acidic hydrolysis. The pH of the extract was adjusted to 1 with H_2SO_4. The extract was then hydrolyzed in an autoclave at 121 °C for 60 min. The insoluble lignin (also called Klason lignin) was filtered from the hydrolyzed extract. The extract was the neutralized to pH 7 with calcium hydroxide ($Ca(OH)_2$) and the gypsum was removed through filtration.

Lactobacillus brevis ATCC367, *Lactobacillus brevis* ATCC8287, *Clostridium acetobutylicum* 6, *Clostridium acetobutylicum* 7 (Berezina et al. 2008) were obtained from the collection of Lononosov Moscow State University. *Clostridium saccharobutylicum* VKPM B-10183 (Berezina et al. 2009), *Clostridium acetobutylicum* VKPM B-4786 and *Bacillus coagulans* VKPM B-10468 were ordered from VKPM (Russian State Collection of Industrial Microorganisms). *Lactobacillus plantarum* DSM 20314 strain was obtained from the Department of Biotechnology and Chemical Technology, School of Chemical Technology, Aalto University, Finland.

Clostridium strains were cultivated at 37 °C in anaerobic flasks in the medium composed of 5 g/L yeast extract, 3 g/L NH_4Ac, 1 g/L KH_2PO_4, 1 g/L $MgSO_4{*}7H_2O$, 0.8 g/L K_2HPO_4, 0.5 g/L cysteine-HCl, 0.05 g/L $FeSO_4{*}7H_2O$, and hydrolyzed larch extract (up to 1 L). *Lactobacillus* and *Bacillus* strains were grown at 30 °C semi-anaerobically (without agitation in closed vials filled with the medium) (Berezina et al. 2010) in the MRS medium composed of 10 g/L casein peptone, 10 g/L meat extract, 5 g/L yeast extract, 1 g/L Tween 80, 2 g/L K_2HPO_4, 5 g/L Na-acetate, 2 g/L ammonium citrate, 0.2 g/L $MgSO_4{*}7H_2O$, 0.05 g/L $MnSO_4{*}H_2O$, and hydrolyzed larch extract (up to 1 L). Kanamycin (12.5 µg/mL) was added in case of *L. brevis*.

The concentration of butanol, ethanol, acetic and butyric acid was measured by a gas chromatograph (GC-2010, Shimadzu, Japan), equipped with a Phase-Stabilwax-DA column (60 m x 0.32 mm x 0.5 mm), a flame ionization detector and nitrogen at 260 °C as carrier gas. i-Butanol was used as an internal standard. Chromatograms were analyzed with the GC-Solution software (Shimadzu, Japan). Monosugars and lactate concentration was quantified with the Waters Alliance HPLC-System equipped with a Waters 2414 detector and a Reprosil-Pur NH_2 column (250 mm x 4.0 mm x 5 μm) (Dr. Maisch GmbH, Germany), at 50 °C with a flow rate of 1 mL/min for 20 min using acetonitrile:H_2O:ethyl acetate (76:20:4).

3.8   Composition analyses

3.8.1   Extractives

The extractives content in wood and pulps was determined according to SCAN-CM 50:94. The air dried wood or pulp was ground to meal (mesh 25-30) and then extracted with acetone with a Soxhlet apparatus. The amount of extractives was then weighed.

3.8.2   Carbohydrates, insoluble lignin and acetyl groups

The carbohydrates, insoluble lignin and acetyl groups in the original wood, extracted wood and pulps were determined according to the standard NREL TP-510-42618 (Sluiter et al. 2008). The carbohydrate analysis was performed by HPAEC (Dionex ICS-3000), using a CarboPac PA20 column and pulsed amperometric detection (PAD). For some pulps the carbohydrates were determined by the method at VTT (Puls et al. 1985; Tenkanen, Siika-aho 2000) and the insoluble lignin was determined according to KCL method 115b:82. For extract samples the carbohydrates were determined following the standard NREL TP-510-42623 or with methanolysis (Holmbom, Örså 1993). The fermented extracts were analyzed by HPLC, Shimadzu (Columbia, MD, USA), using an Aminex HPX-87H (H) column with RI (refractive index) and UV (ultraviolet) detection.

3.8.3   Soluble lignin

Soluble lignin in wood and in extracts was generally determined according to TAPPI UM 250, i.e. at 205 nm using an extinction coefficient of 110 L/g cm. In

the first composition analyses the soluble lignin in the extract was, however, determined at 280 nm using the extinction coefficient 24.3 L/g cm (Alén, Hartus 1988). Calculation of the lignin content did not take into consideration the possible contribution of furan derivatives to the adsorption at 280 nm.

3.8.4 Dry solids and ash

The dry solids content of the extract and wash water samples was determined by drying a sample at 105 °C overnight. The dry solids content of the black liquor samples was determined according to SCAN-N 22:96. The ash content in black liquor was determined by burning the sample in a muffle furnace at 700 °C (KCL 59:83). In wood samples ash was determined by the NREL TP-510-42622.

3.8.5 Furfural, HMF, acetic acid, formic acid

Furfural and HMF (hydroxymethylfurfural) were determined by HPLC (Dionex Ultimate 3000 (Sunnyvale, CA, USA), Acclaim OA column, Diode array detector). Acetic acid and formic acid in extracts and extracted chips were determined with analytical assay kits from Megazyme International (Megazyme International 2010).

3.8.6 Other compounds

Total sodium (Na) and sulfur (S) were determined according to a KCL internal method. The uronic acid groups in the original and extracted wood were determined according to an improved methanolysis-GC method (Alves et al. 2010), except that the evaporation was done in a rotavap equipment. The nitrogen content in wood was analyzed by the method CEN/TS 15104:2005 (Nab Labs Oy, Rauma, Finland). The total organic carbon (TOC) in extracts was determined according to standard SFS-EN 1484 using a Shimadzu TOC-5000A.

3.8.7 Reproducibility and variations

Generally, the analyses were performed in duplicates. If the deviation was large, then the analysis was repeated. In larger series variations and errors can easily be noticed, and then the analysis of this specific sample can be repeated. The standard deviation was less than 5% in the composition analyses, except for the ash determination where the deviation occasionally was as high as 10 %.

3.9 Process evaluation

3.9.1 Technical evaluation

Steady-state material and energy balance process models were produced using WinGEMS V.5.3 (Metso 2012). This process simulation software was originally developed for the pulp and paper industry and has specialty blocks and unit operations (i.e. solid/liquid handling washing and separation) critical for modeling of biomass based processing technologies. Once the WinGEMS model converged on a steady-state solution, data related to pulp and lactic acid production, chemical usage, and electricity balance were collected as output from the simulation. Input data for the simulation was mainly taken from the experimental results. Some parts of the process model were constructed based on information taken from literature (Datta 1995; Glassner, Datta 1990; Lee et al. 1998; Smith, Sanders 1977) and equipment producers (Andritz 2012).

3.9.2 Economic evaluation

Information about cost and prices was collected from the literature, market reports, equipment producers and discussions with experts. The consumptions and production values were taken from the simulation results. General assumptions were made, operating costs estimated and revenues calculated. Two slightly different larch biorefinery processes were compared to a conventional larch kraft process. The cash flow was determined in order to analyze the different cases. Sensitivity analyses were also performed. Investment costs were estimated. By comparing the cash flow with the estimated investment costs, the profitability of a larch biorefinery could be determined.

4   RESULTS AND DISCUSSION

4.1   Characteristics of the Siberian larch wood chips (Paper I)

The dry matter content of the larch chips was 60%, and the basic density 466 kg/m³. Siberian larch wood contains about 72% carbohydrates on wood (glucan 40%, xylan 5%, galactan 13%, arabinan 3%, and mannan 11%), about 25% lignin and a small amount of extractives, about 2%. Furthermore, *Larix sibirica* contains 1% acetyl groups and 0.5% ash. All these numbers are given on original dry wood basis and the values for the separate sugars are given in anhydromonomeric form. The composition determined in this study is in accordance with values in the literature (Nevalainen, Hosia 1969a; Sjöström 1993). The mannan content of the present larch wood chips was somewhat higher compared to the values given by Nevalainen and Hosia.

4.2   Pre-extraction of wood chips (Paper I, II, III)

4.2.1   Extraction yield

The yields from all pre-extraction (PE) trials performed within this study are presented in **Figure 2**. The trials show that the yield decreases with increasing PE temperature and time. The extraction yield at 140 °C or below is of the order of 10%, but increases to about 20% at 160 °C. PE at 160 °C for 60 min had a weight loss of 17.5%, whereas a study where loblolly pine was pre-extracted under similar conditions resulted in a weight loss of 7.9% (Yoon et al. 2008). Thus, as expected, more material dissolves out of arabinogalactan containing Siberian larch than from loblolly pine which contains galactoglucomannan as the main hemicellulose component.

4.2.2   Mass balance of pre-extraction

Mass balances for water pre-extraction (PE) at different conditions are presented in **Table 4**. The first mass balance presented is based on extraction yield and the dry solids yield. The extraction yield and dry solids yield sum up to percentages based on
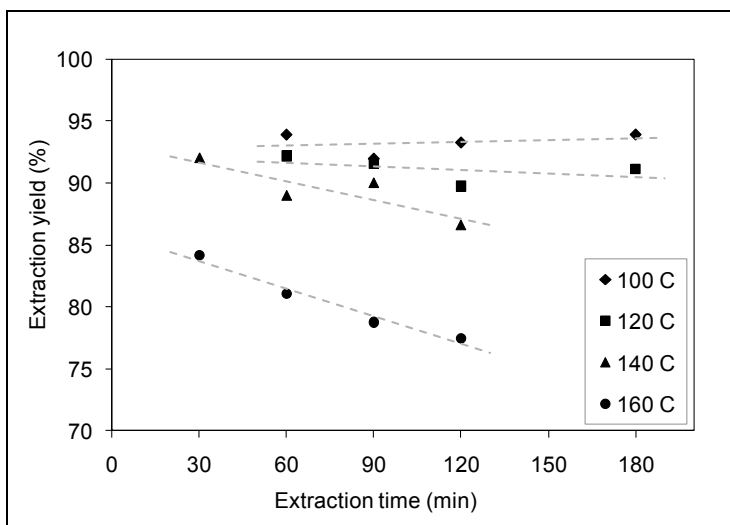
Figure 2 Yields from pre-extraction (PE) trials.

original wood varying from 95.9% to 99.4%, with a slightly decreasing trend at stronger extraction conditions. This may be explained by volatilization of low-boiling dissolved components (acetic acid, formic acid, furfural etc.) during the dry solids analysis of the extracts and thorough washing of the chips after extraction. Evaporation of the volatile components during the dry solids determination is also seen, when comparing the dry solids yield to the total analyzed components in the extract, which are generally slightly higher.

The component composition of the extracted wood and the extracts are given below the yield balance in **Table 4**. Also included is the composition of the original larch wood. The mass balance includes carbohydrates, lignin, extractives and other compounds (i.e. acetyl groups and ash) for wood, and carbohydrates, lignin and by-products for the extracts. The following by-products were analyzed in the extracts; acetic acid, formic acid, furfural and HMF. The values for the sugars are given in anhydro-monomeric form. The wood analyses were made on pre-extracted, washed and dried wood, from which extractives have been removed. The amount of dissolved wood in the extract was calculated using the density and the dry solids of the extract, after which the composition of the extracts could be given as % on wood. The overall mass balance based on composition analyses is complete from 97.4% to 101.2%. It can also be seen that the summative analysis of the extracted wood is closely equal to that of the mass yield.

Table 4 Mass balance for water pre-extraction of Siberian larch (*Larix sibirica*). Values given as % on wood and for the sugars in anhydro-monomeric form.

Ext temp., °C	Orig. wood	Water extraction								
		100	100	120	120	140	140	160	160	160
Ext time, min		60	90	60	90	60	90	30	60	90
Extract pH		5.4	5.2	4.7	5.1	4.6	4.6	4.4	3.9	3.9
Extract density, g/cm3		1.004	1.002	1.002	1.003	1.008	1.008	1.010	1.013	1.018
Mass balance based on yields:										
Extraction yield		94.5	92.8	90.8	91.7	88.3	89.9	84.2	82.5	79.9
Dry solids yield		4.9	5.1	5.8	6.7	7.6	9.2	12.1	14.4	16.9
Total		**99.4**	**97.9**	**96.6**	**98.4**	**95.9**	**99.1**	**96.2**	**97.3**	**96.8**
Mass balance based on composition analyses:										
Extract										
Carbohydrates		4.8	4.8	5.9	6.6	7.8	9.0	11.3	13.0	16.2
Arabinose		0.7	0.7	0.8	1.0	1.4	1.8	2.1	2.0	2.0
Galactose		4.0	4.0	4.9	5.4	6.0	6.6	7.2	7.9	10.2
Glucose		0.1	0.1	0.1	0.1	0.2	0.2	0.4	0.5	0.7
Xylose		0.0	0.0	0.0	0.0	0.1	0.1	0.6	0.9	1.1
Mannose		0.0	0.0	0.0	0.0	0.1	0.2	1.0	1.6	2.2
Monomeric sugars		0.2	0.2	0.2	0.2	0.4	0.8	1.4	1.9	2.5
Oligomeric sugars		4.7	4.7	5.7	6.4	7.3	8.2	9.9	11.1	13.7
Lignin		0.1	0.1	0.4	0.4	0.6	0.7	0.9	1.1	1.2
Byproducts		0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.7	0.8
Acetic acid, free		0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.2
Acetic acid, bound		0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.2	0.3
Formic acid		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Furfural		0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.2	0.2
HMF		0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1
Total in extract		**5.0**	**5.1**	**6.4**	**7.2**	**8.5**	**10.0**	**12.6**	**14.7**	**18.2**
Wood										
Carbohydrates	71.7	68.9	65.8	65.3	63.6	62.4	60.5	58.1	57.1	53.5
Arabinose	2.9	2.3	1.9	2.3	1.9	1.4	1.2	0.3	0.2	0.2
Galactose	12.8	8.6	8.1	8.1	8.4	6.4	7.3	5.0	4.6	4.2
Glucose	39.9	41.1	40.1	38.6	38.2	38.9	37.5	40.3	39.2	37.7
Xylose	5.0	4.9	4.7	4.9	4.5	4.7	4.3	3.7	3.8	3.2
Mannose	11.1	11.8	11.0	11.4	10.5	10.9	10.1	8.8	9.2	8.0
Lignin	24.9	24.7	24.1	25.1	25.7	24.6	25.2	24.6	24.8	24.2
Extractives	1.8	1.3	1.1	1.3	1.1	1.4	1.3	1.7	1.7	1.7
Other	1.4	1.3	1.3	1.3	1.2	1.2	1.0	1.0	1.0	0.8
Acetyl groups	0.9	0.9	0.9	0.9	0.9	0.9	0.8	0.8	0.8	0.7
Ash	0.5	0.4	0.4	0.4	0.3	0.3	0.2	0.2	0.2	0.2
Total in wood	**99.8**	**96.2**	**92.3**	**93.1**	**91.6**	**89.6**	**88.0**	**85.3**	**84.6**	**80.2**
Total carbohydrates	71.1	73.8	70.6	71.2	70.2	70.1	69.5	69.4	70.1	69.7
Total	**99.8**	**101.2**	**97.4**	**99.5**	**98.7**	**98.1**	**98.0**	**98.0**	**99.4**	**98.4**

The uronic acids (more specifically carboxylic groups at the C_6 atom of sugar units) were not determined for all wood samples and are therefore not included in this mass balance. The uronic acid content for certain wood samples is presented in **Table 5**. With uronic acid groups added the overall mass balance slightly exceeds 100% for the original wood. This is likely due to a small systematic analysis error in the component analysis.

Siberian larch wood contains about 70% carbohydrates, 25% lignin and a small amount of extractives. During the strongest extraction conditions (160 °C and 90 min) about 16% of carbohydrates as anhydro-monomeric sugars are quantified in the extract compared to about 19.6% (= 99.8% - 80.2%) based on the difference between the extracted wood and original wood. The lignin content of this extract is about 1.2% (= 24.9% – 23.7%) which is the same as that based on the wood analysis. The amount of other components (acetyl groups, formic acid and furfural) present in the extracts is relatively small, below 1%.

4.2.3   Influence of extraction temperature and time

More wood material is dissolved with increasing extraction temperature and time (**Figure 3a**). The extracts mainly consist of galactan. At temperatures up to and including 120 °C only galactan and arabinan are dissolving as oligomers, but at higher temperature xylan and mannan oligomers also appear in the extracts, and hydrolysis of the oligomers to monomers become significant. The finding that only arabinogalactan dissolves at 120 °C or lower can be explained by its high solubility (Sjöström 1993). At 160 °C, the extracts contain a significant amount of mostly oligomeric glucomannan and xylan. Thus to preserve these hemicelluloses in the extracted wood, the ideal extraction temperature would be about 140 °C to 150 °C.

Simultaneously, also more by-products are produced with stronger extraction conditions (**Figure 3b**), for example, the yield at 160 °C for 90 min was the highest (0.8%). The by-products in this extract are mostly HMF and furfural, 0.4% and 0.2%, respectively. A small amount of acetic acid (0.1% on wood or about 10% of the original acetyl groups) appears in the 140 °C extracts. In the 160 °C extract this increases further to 0.4% on wood, an amount, which is still relatively small compared to that found for hardwood extracts (Tunc, van Heiningen 2008).
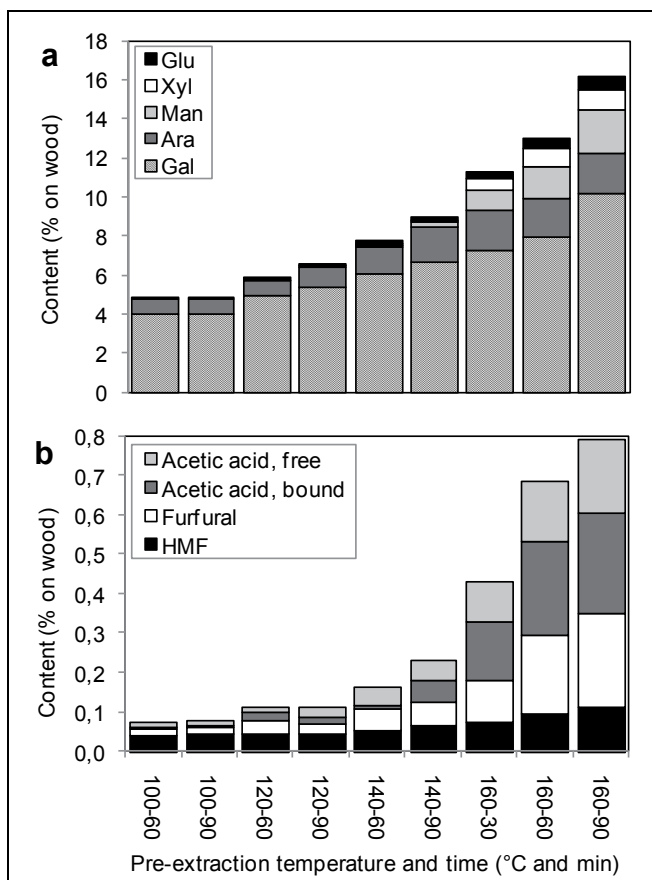
Figure 3 Sugar content (a), and by-products and acetic acid (b) in water extracts of Siberian larch (*L. sibirica*).

The acetic acid in the extracts is either in free form or bound to the dissolved oligomers as an acetyl group. There is an increase in the deacetylation of the wood, when the pre-extraction temperature is increased from 140 °C to 160 °C. This is reflected in the pH of the extract of 4.6 and 3.9, respectively. The dissolved lignin content is also somewhat correlated with the stronger acidity, and increases from 0.7% at 140 °C and 90 min to 1.2% at 160 °C and 90 min. This increase may be important because it is known that the lignin removed during autohydrolysis leads to formation of sticky lignin precipitates in the digester and extract processing equipment (Leschinsky et al. 2007).

Uronic acids and nitrogen content were determined for the original wood and some of the extracted wood samples. The nitrogen content in original wood and extracted wood is low, i.e. below 0.1%. The content of uronic acid groups,

occurring in galacturonic acid (GalA), methylglucuronic acid (MeGlcA), and glucuronic acid (GlcA), is presented in **Table 5**. The amount of uronic acid groups in the original wood is about 3.9% and was found to decrease in the extracted wood. This is due to elevated degradation rate of uronic acid groups at higher temperatures (Leschinsky et al. 2009). The degradation is caused by dissolution of the methylglucuronic acid groups attached to dissolved xylan oligomers as well as galacturonic acid originating from pectins, and also by decarboxylation of uronic acids.

Table 5 Uronic acid groups in original wood and extracted chips as % on wood.

Ext temp., °C Ext time, min	Original wood	Extracted chips	
		140 90	160 90
GalA	2.2	1.3	0.4
MeGlcA	1.3	1.1	0.6
GlcA	0.4	0.3	0.3
Total	**3.9**	**2.7**	**1.3**

The total organic carbon (TOC) results and dry solids yields of some extracts are presented in **Table 6**. The TOC content in the extracts increases with stronger pre-extraction conditions nearly exactly proportional to the dry solids yield of the extracts listed. Comparison of the two values shows that about 41% of the dissolved wood material is organic carbon. This is equivalent to a ratio between the dry solids yields and the TOC of 2.4 ± 0.1, which is in between the calculated value of high DP (degree of polymerization) arabinogalactan of 2.2 and that of galactose of 2.5. These calculated values present the molar weight of the sugar relative to the molar weight of carbon in the sugar. Arabinogalactan is assumed to have 1:4 molar ratio (see extract in **Table 4**). This gives the formula $C_5(H_2O)_4+$

Table 6 TOC content and dry solids (DS) yield of certain extract samples as % on wood.

Ext temp., °C Ext time, min	Water extraction						Ave	StDev
	100 90	120 90	140 60	140 90	160 60	160 90		
TOC	2.1	2.7	3.3	3.9	5.8	6.8		
Dry solids yield	5.1	6.7	7.6	9.2	14.8	16.9		
TOC/DS, %	40.9	40.2	42.8	42.5	39.1	40.0	40.9	1.5
DS/TOC	2.4	2.5	2.3	2.4	2.6	2.5	2.4	0.1

$4(C_6(H_2O)_5$, and the following calculation $(29*12+24*18)/29*12=2.24$. The formula for galactose is $C_6(H_2O)_6$, which gives the following calculation $(6*12+6*18)/(6*12)=2.5$.

4.2.4 The water extract from PE at optimal conditions (150 °C/ 90 min)

The composition of water extract from pre-extraction at 150 °C for 90 min is presented in **Table 7**. Compared to the 160 °C/ 90 min extract this extract has somewhat lower sugar content (11.2% versus 16.2% on wood). The increased dissolution of sugar is mainly caused by galactose (7.2% versus 10.2%) and mannose (1.0% versus 2.2%), but also xylose starts to dissolve more at the higher temperature (0.6% versus 1.1%). Ideally, only the water-soluble hemicelluloses (arabinogalactan) would be removed from the wood chips through water pre-extraction, while the other hemicelluloses (xylan and glucomannan) would rather remain in the wood chips and pulp. This is the basis for selecting that the pre-extraction temperature of 150 °C is optimal for this kind of a larch biorefinery.

Table 7 Composition of water extract from pre-extraction of *Larix sibirica* at 150 °C/ 90 min.

	Extract (150 C/ 90 min)	
Volume, mL	630	
pH	4.0	
Density, g/cm3	1.025	
Dry solids, % on wood	12.4	
	g/L	% on wood
Carbohydrates	31.0	11.2
Ara	5.7	2.0
Gal	19.9	7.2
Glu	1.0	0.4
Xyl	1.7	0.6
Man	2.7	1.0
Monomeric sugars	3.89	1.4
Oligomeric sugars	27.1	9.8
Lignin	2.1	1.1

4.3 Washing efficiency (Paper III)

300 g o.d. wood chips containing 200 mL water was charged to the pre-extraction together with 850 mL fresh water. After the pre-extraction, about 630 ± 10 mL of extract with about 12% dissolved wood (dry solids) was drained out from the chips, while 420 mL extract remained in the extracted chips. In other words,

about 3/5 of the extract was drained. **Table** 8 describes the inputs and outputs of pre-extraction and of the three different washing cases; no, mild, and extensive washing. The not-washed extracted chips were centrifuged before pulping. In the mild wash case, 630 mL fresh water was added to the washing. For extensive washing the volume of fresh water used for washing was significantly larger (35 L). The extracted and washed chips were centrifuged. In the case of mild washing about 720 mL of wash water containing about 4% dissolved wood (dry solids) was removed. The chips contained about 330 mL water, when they entered the pulping stage.

Depending on the type of washing, different amounts of wood were charged with the pre-extracted wood to pulping. More dissolved solids were removed with more washing. Therefore, less washing of pre-extracted chips results in larger amounts of dissolved solids entering pulping. The dissolved solids consume chemicals during pulping and should therefore be removed before the cooking stage.

Based on the data in Table 8, amounts of wood removed and washing characteristics can be calculated. 7.4% on wood was removed by pre-extraction, 8.5% on wood by PE and centrifugation, and 11.4% on wood by PE, mild wash and centrifugation. The percentage collected dissolved wood compared to that dissolved during PE was also determined. The washing is described by a dilution factor and washing efficiency. The dilution factor describes the volume of fresh water (L) added per amount of wood charged to washing (0.3 o.d. kg). The dilution factor for the no wash was 0, for the mild wash 2, and for the extensive wash 117, respectively. The washing efficiency is described by comparing the percentage of dissolved wood solids in the removed wash waters to the maximum removable amount for each washing case. For extensive washing, the washing efficiency was 100% and for mild washing, it was 69%.

The characteristics and compositions of the larch extract and of the wash water obtained from the mild wash of the pre-extracted chips are presented in **Table 9**. The sugars are reported as anhydrosugars, i.e. as originally present in larch. The liquid volume collected after PE at 150 °C for 90 min was 630 mL with a density of 1.025 kg/L. 7.4% on wood dissolved wood (dry solids) was removed by drainage. The total sugars in the collected extract represents 6.7% based on the original oven dry wood, mainly arabinogalactan.

Table 8 Material flows for pre-extraction (PE) and three different types of washing of pre-extracted chips of Siberian larch.

	PE (150 C/ 90 min) L/W 3.5		No wash		Mild wash L/W 3.5		Extensive wash L/W ∞	
	Wood %	Liquid mL	Wood %	Liquid mL	Wood %	Liquid mL	Wood %	Liquid mL
IN to PE or wash								
Wood	100	200		420		420		420
Additional water		850		0		630		35000
Before drainage								
Liquid phase	12.4	1050		420	5.8	1050	max	35420
OUT								
Drainage	7.4	630	1.1		3.5	630		35000
Centrifugation				90	0.5	90		90
Drainage+Centrif.					4.0	720	max	35090
PE+Wash, % on wood			7.4+1.1 = 8.5		7.4+4.0 = 11.4			
Removed/Dissolved, %	7.4/12.4*100 = 60		8.5/12.4*100= 69		11.4/12.4*100 = 92			
Dilution factor, L/kg			0/0.3 = 0		0.63/0.3 = 2		35/0.3 = 117	
Washing efficiency, %					4.0/5.8*100= 69		max/max*100 = 100	

Drainage leaves about 420 mL of liquid in wood. Centrifugation leaves about 330 mL of liquid in wood.

PE+Wash=Removed wood by PE+Removed wood from wash

Removed/Dissolved=Wood totally removed by PE and washing/Wood dissolved in PE

Dilution factor=Volume of wash water/Amount of original wood

Washing efficiency=Removed wood during current washing/Amount possible to remove*100

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Table 9 Characteristics of larch extract, wash water and the combined stream. The extract is from water pre-extraction at 150 °C for 90 min, and the wash water is from mild washing of the pre-extracted chips.

	Extract (150 C/ 90 min)				Wash water (Mild wash)				Combined stream (Ext+Ww)
Total volume, mL	1050				1050				
Collected volume, mL	630	*Drainage*			720	*Drainage and centrifugation*			1350
pH	4.0				4.1				4,1
Density, g/cm3	1.025				1.002				1.013
	Conc. g/L	Amount g	Collected % on wood	Total % on wood	Conc. g/L	Amount g	Collected % on wood	Total % on wood	Collected % on wood
Dry solids	35.5	22.3	7.4	12.4	16.6	12.0	4.0	5.8	11.4
Carbohydrates	31.0	19.5	6.7	11.2	13.9	10.0	3.4	5.0	10.2
Ara	5.7	3.6	1.2	2.0	2.5	1.8	0.6	0.9	1.8
Gal	19.9	12.6	4.3	7.2	8.3	6.0	2.1	3.0	6.4
Glu	1.0	0.6	0.2	0.4	0.5	0.4	0.1	0.2	0.3
Xyl	1.7	1.1	0.4	0.6	1.0	0.7	0.2	0.4	0.6
Man	2.7	1.7	0.6	1.0	1.6	1.2	0.4	0.6	1.0
Monomeric sugars	3.9	2.5	0.8	1.4	2.8	2.0	0.5	0.8	1.4
Oligomeric sugars	27.1	17.1	5.9	9.8	11.1	8.0	2.9	4.2	8.8
Lignin	2.1	1.3	0.4	0.7	0.6	0.4	0.1	0.2	0.6

Assuming that the amount of remaining water has the same total dissolved sugar concentration leads to a total dissolved sugar amount of 11.2% (collected 6.7%) on wood and a total solids content on wood of 12.4% (collected 7.4%). Mild washing removes an additional 3.4% of carbohydrates, giving a total carbohydrate removal of 10.2% in the combined extract and wash water. Comparison of the latter number with the calculated total dissolved amount of sugar of 11.2% suggests that after washing, about 9% (= (11.2-10.2)/11.2*100) of the dissolved sugars remain in the wood chips. This percentage is higher for lignin, about 14% (= (0.7-0.6)/0.7*100), most likely because of slower diffusion of the dissolved lignin. Finally it can be seen that the amount of sugars plus lignin in the extract and wash water are somewhat lower than the dry solids contents, i.e. 7.1% (= 6.7 + 0.4) and 3.5% (= 3.4 + 0.1), compared to 7.4% and 4.0%, respectively.

4.4   A variety of larch pulping trials

Here are the results of several different larch pulping trials presented. These cooks were conducted under different conditions (i.e. H-factor, alkali charge and sulfidity) in order to receive pulps of different kappa numbers. The influences of PS and AQ were tested, as well as the influence of pre-extraction prior cooking.

4.4.1 Kraft pulping

Table 10 presents both the pulping conditions and the pulp and black liquor properties for the kraft pulping trials. The H-factor varied from 850 to 1850 h, the effective alkali from 19 to 23%, and the sulfidity was between 35 and 37%. By increasing the effective alkali charge, lower kappa numbers are reached at the same H-factor. Higher alkali charge also results in lower viscosity of the pulp. The pulp yield is about 40% for kappa number 26.

Table 10 Conditions, pulp and black liquor properties for kraft pulping of Siberian larch (L/W 3.5, heat-up time 60 min, 167 °C).

	Kraft pulping								
Cooking									
H-factor, h	850	1250	1650	850	1250	1650	1250	1650	1850
Effective alkali charge, %	19	19	19	20	20	20	20	23	23
Sulfidity of white liquor, %	35.0	35.0	35.0	35.0	35.0	35.0	36.3	37.6	37.6
Pulp									
Yield, %	43.2	42.9	41.3	43.3	41.1	40.2	41.5	40.4	40.2
Reject, %	0.8	0.7	0.3	0.9	0.5	0.3	0.5	0.1	0.1
Kappa number	50.3	38.1	31.7	47.1	33.7	28.6	31.4	26.1	24.2
Viscosity, mL/g	1130	1160	1060	1150	1090	1040	1100	941	882
Black liquor									
pH	13.3	13.2	13.1	13.3	13.2	13.2	13.2	13.3	13.1
Residual alkali, g NaOH/L	10.1	7.6	6.8	12.0	9.9	8.7	10.3	11.9	10.8

4.4.2 PS pulping

The conditions and properties from the PS pulping, i.e. pulping with polysulfide are presented in **Table 11**. The PS charge used is 2% in all cases. The H-factor varies from 850 to 1650 h, and the effective alkali is 20-22%. It can be seen that with 2% PS addition the pulp yield increases. The pulp yield for the PS pulp for kappa number 26-27 is 42%, which is higher than 40% for the regular kraft pulp (**Figure 4**).

Table 11 Conditions, pulp and black liquor properties for kraft pulping with polysulfide (PS) of Siberian larch (L/W 3.5, heat-up time 60 min, 167 °C).

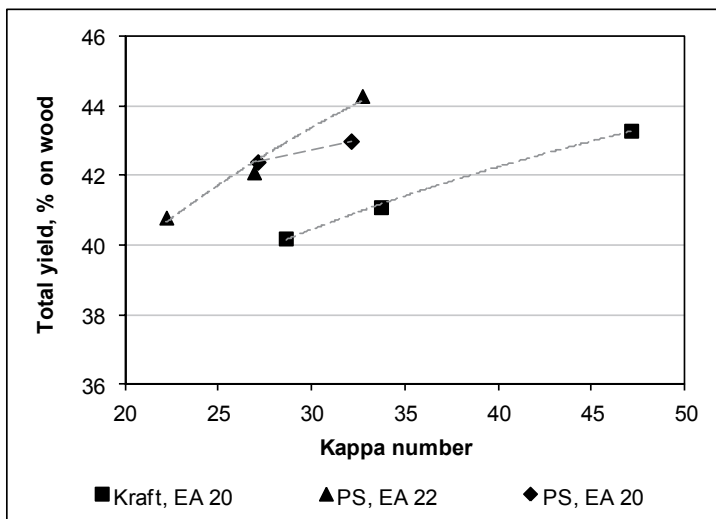|	PS pulping						
Cooking							
H-factor, h	1250	1650	850	1650	850	1250	1650
Effective alkali charge, %	20	20	21	21	22	22	22
Polysulfide charge, %	2	2	2	2	2	2	2
Sulfidity of white liquor, %	36.3	36.3	36.5	36.5	36.3	36.3	36.3
Sulfidity of PS liquor, %	38.6	38.6	39.2	39.2	38.6	38.6	38.6
NaOH addition, %	1.7	1.7	2.1	2.1	1.7	1.7	1.7
Pulp							
Yield, %	43.0	42.4	43.0	41.8	44.3	42.1	40.8
Reject, %	0.4	0.2	0.4	0.2	0.9	0.3	0.1
Kappa number	32.1	27.1	37.0	27.2	32.7	26.9	22.2
Viscosity, mL/g	1140	1100	1150	1040	1140	1070	1000
Black liquor							
pH	13.0	12.9	13.3	13.1	13.2	13.2	13.1
Residual alkali, g NaOH/L	6.4	5.7	10.2	6.6	11.0	9.2	9.0

Figure 4 Total pulp yield versus kappa number for kraft and PS pulping.

Table 12 Conditions, pulp and black liquor properties for PE-Kraft pulping of Siberian larch (Pre-extraction: L/W 3.5, 160 °C for 60 min, heat-up time 65 min; Washing: extensive; Cooking: L/W 3.5, heat-up time 60 min, 167 °C).

	PE-Kraft pulping						
Cooking							
H-factor, h	850	1250	1650	850	1250	1650	1250
Effective alkali charge, %	16	16	16	17	17	17	17
Sulfidity of white liquor, %	35.2	35.2	35.2	35.2	35.2	35.2	35.4
Pulp							
Yield, %	37.3	36.0	34.8	36.3	35.9	34.5	35.5
Reject, %	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Kappa number	48.0	33.2	24.9	40.8	27.9	22.4	25.1
Viscosity, mL/g	1210	1150	1030	1190	1050	960	1090
Black liquor							
pH	13.2	13.1	13.1	13.3	13.2	13.2	13.2
Residual alkali, g NaOH/L	8.3	7.1	6.5	11.4	8.7	8.5	10.0

4.4.3 PE-Kraft pulping

Table 12 presents the conditions for cooking after pre-extraction (PE) at 160 °C for 60 min. Here, PE at 160 °C for 60 min dissolved 16.6% of the wood material (**Paper I**). The removal of a significant part of wood hemicelluloses due to PE allows a lower alkali charge in the subsequent kraft cooking process since

hemicelluloses consume most of the alkali during cooking. PE also allows a reduction in the H-factor. Naturally, the removal of hemicelluloses results in pulp yield loss. The pulp yield for pulps of kappa number 25-27 after PE is only about 35%, which can be compared to the pulp yield of about 40% for not pre-extracted kraft pulps. Again lower kappa numbers can be reached by using higher effective alkali charges. The viscosity is not affected by the PE.

4.4.4 PE-PS pulping

The conditions and properties for the pre-extraction (PE) PS pulping experiments are presented in **Table 13**. H-factors vary from 850 to 1650 h, the effective alkali charge is 17%, and the PS charge is 2 or 4%. At higher PS charges more NaOH has to be added in order to compensate for the consumption of hydroxyl ions. The effect of the higher PS charge can be observed by comparing the pulp yields. Pulp with kappa number 26-27 has a yield of about 37% at PS charge 2%, while it increases to about 39% at PS charge 4%. However a PS charge of 4% is considered

too high for practical implementation. The viscosity slightly increases with higher PS charge. The residual alkali in the black liquor is lowest in the PS 4% cases, in agreement with the largest delignification at this higher PS charge.

Table 13 Conditions, pulp and black liquor properties for PE-PS pulping of Siberian larch (Pre-extraction: L/W 3.5, 160 °C for 60 min, heat-up time 65 min; Washing: extensive; Cooking: L/W 3.5, heat-up time 60 min, 167 °C).

	PE-PS pulping							
Cooking								
H-factor, h	850	1250	1650	1250	1650	850	1250	1650
Effective alkali charge, %	17	17	17	17	17	17	17	17
Polysulfide charge, %	2	2	2	2	2	4	4	4
Sulfidity of white liquor, %	36.5	36.5	36.5	35.4	35.4	35.4	35.4	35.4
Sulfidity of PS liquor, %	40.0	40.0	40.0	38.8	38.8	44.5	44.5	44.5
NaOH addition, %	2.4	2.4	2.4	2.1	2.1	4.9	4.9	4.9
Pulp								
Yield, %	38.1	37.1	35.5	36.8	36.2	39.1	38.8	37.0
Reject, %	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.1
Kappa number	39.5	31.9	22.9	26.9	21.1	32.6	27.5	21.4
Viscosity, mL/g	1240	1160	1050	1150	1090	1250	1180	1130
Black liquor								
pH	13.2	13.1	13.1	13.0	13.0	13.0	12.8	12.8
Residual alkali, g NaOH/L	7.4	5.9	5.9	6.3	5.3	4.9	3.8	3.8

4.4.5 PE-PSAQ pulping

Detailed information about the conditions and the pulp and liquor properties in the PE-PSAQ pulping case is presented in **Table 14**. The H-factors were from 650 to 1450 h, the effective alkali charge was 17%, and the PS charge was 4%. The AQ charge was either 0.05 or 0.1%. The pulp yield for kappa number 26 can be estimated to be about 39%, which is almost the same as the yield of the kraft pulp 40%. Thus the yield loss caused by the pre-extraction was almost compensated by using PS and AQ as pulping additives. The viscosity of the PE-PSAQ pulp of kappa number 26 is about 1170 mL/g, compared to about 940 mL/g for the regular kraft pulp of kappa number 26 (**Table 10**). The significant improvement in intrinsic viscosity is in part due to the much lower effective alkali charge (17% versus 23%) in PE-PSAQ cooking.

Table 14 Conditions, pulp and black liquor properties for PE-PSAQ pulping of Siberian larch (Pre-extraction: L/W 3.5, 160 °C for 60 min, heat-up time 65 min; Washing: extensive; Cooking: L/W 3.5, heat-up time 60 min, 167 °C).

	PE-PSAQ pulping					
Cooking						
H-factor, h	650	1050	1450	650	1050	1450
Effective alkali charge, %	17	17	17	17	17	17
Polysulfide charge, %	4	4	4	4	4	4
Anthraquinone charge, %	0.05	0.05	0.05	0.1	0.1	0.1
Sulfidity of white liquor, %	36.7	36.7	36.7	36.7	36.7	36.7
Sulfidity of PS liquor, %	45.6	45.6	45.6	45.6	45.6	45.6
NaOH addition, %	4.9	4.9	4.9	4.9	4.9	4.9
Pulp						
Yield, %	40.3	40.3	38.3	41.8	39.5	38.0
Reject, %	0.3	0.2	0.0	0.3	0.2	0.1
Kappa number	41.1	32.8	24.8	42.6	30.2	23.8
Viscosity, mL/g	1220	1210	1120	1220	1180	1080
Black liquor						
pH	13.0	12.9	12.8	13.0	12.9	12.8
Residual alkali, g NaOH/L	5.9	3.9	3.8	5.7	4.8	4.0

4.5   Comparison of pulping methods (Paper I)

The different pulping methods are here being compared by presenting pulps with similar kappa numbers, but different production processes (**Table 15**). Pulps with kappa numbers between 26 and 30 have been selected for the comparison. The basic pulp properties are presented and compared. Moreover, also the carbohydrate, lignin, extractives, dry solids, sodium and sulfur content are considered.

Anthraquinone (AQ) is known to accelerate the delignification rate at a given H-factor, and that is why a shorter cooking time is required for the PSAQ cook. However, the typical influence of AQ on the delignification behavior could not be observed at the high charge of PS of 4% (**Figure 5**).

Table 15 Pulps with kappa number 26-30. Pulp and black liquor properties from kraft, PS and PSAQ pulping without/with PE 160 °C/ 60 min of Siberian larch.

|	Kraft	PS	PE-Kraft	PE-PS	PE-PSAQ
Cooking					
H-factor, h	1650	1250	1250	1250	1050
Effective alkali charge, %	20	22	17	17	17
Polysulfide charge, %		2.1		4	4
Anthraquinone charge, %					0.1
Sulfidity of white liquor, %	35.0	36.3	35.2	35.4	36.7
Sulfidity of PS liquor, %		38.6		44.5	45.6
NaOH addition, %		1.7		4.9	4.9
Pulp					
Kappa number	28.6	26.9	27.9	27.5	30.2
Total yield, % on wood	40.2	42.1	35.9	38.8	39.5
Reject, % on wood	0.3	0.3	0.1	0.1	0.2
Viscosity, mL/g	1040	1070	1050	1180	1180
Carbohydrates	32.2	35.1	27.9		32.1
Glucan	26.8	29.3	25.8		28.2
Xylan	2.6	2.3	1.0		1.3
Galactan	0.3	0.3	0.1		0.2
Arabinan	0.2	0.2	0.0		0.0
Mannan	2.4	2.9	1.0		2.4
Lignin	4.4	4.2	4.0		4.6
Extractives	1.8	1.5	1.4		1.5
Black liquor					
Residual alkali, g NaOH/L	8.7	9.2	8.7	3.8	4.8
pH	13.2	13.2	13.2	12.8	12.9
Dry solids, % on wood	21.2	22.3	17.0		17.5
Total Na, %	17.3	18.4	18.3		19.3
Total S, %	4.7	6.9	5.0		9.8
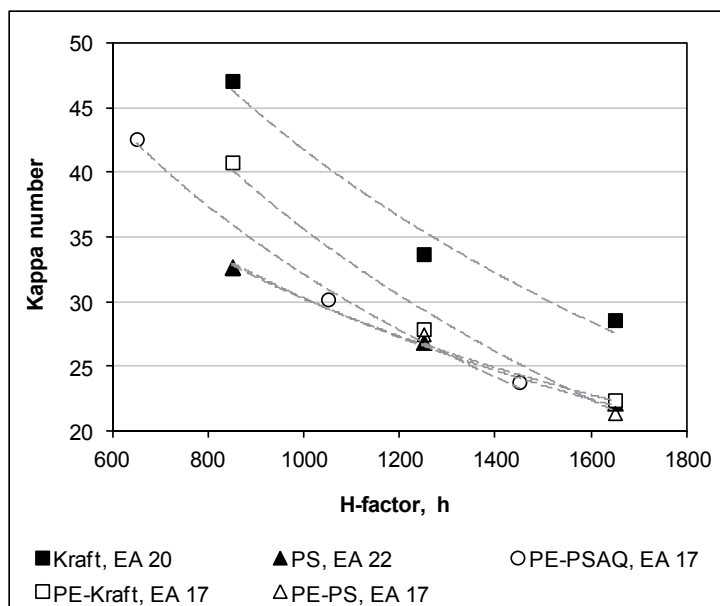
Figure 5 Kappa number of Siberian larch laboratory unbleached kraft pulp as a function of H-factor. Different kraft cooks and pre-extraction (PE) kraft cooks with polysulfide (PS) and anthraquinone (AQ) were conducted at 167 ºC and H-factors of 850-1650 h. The H-factors for the pre-extraction PSAQ cooks were 650-1450 h. Pre-extraction temperature of 160 ºC and time of 60 min were used.

The total yield of different unbleached kraft and pre-extraction (PE) kraft pulps of larch wood are illustrated in **Figure 6** as a function of kappa number. The total yield of PE-Kraft cooks is 4-6% lower than that of conventional larch kraft cooks without PE. A significant yield loss is to be expected after extracting 16.6% (**Paper I**) of the wood during PE (160 ºC for 60 min). The total yield of pre-extracted kraft pulp at kappa number 30 was about 5%-units lower than that of conventional larch kraft pulp at the same kappa number. The reject content was low for all pulps. The yield of the larch kraft pulp in this study was relatively low (about 41.5% at kappa number 35) compared to values reported in literature for larch, pine and spruce, where the total yield for unbleached kraft pulps of kappa number 35 were 46.5%, 48.0% and 50.0% (Nevalainen, Hosia 1969b).

The results in **Figure 6** also show that conventional kraft cooking with PS increases the yield by about 2% as expected, with higher increases at higher pulp kappa numbers. At kappa number 30 the total yield of pre-extracted kraft pulp with 4% PS was about 3.5% higher than pre-extracted conventionally kraft pulp. However, it is still about 2% lower than non-extracted conventional larch kraft

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pulp. The yield gain at 30 kappa obtained at 4% PS in pre-extraction pulping is similar to that of 2% PS in conventional kraft pulping.
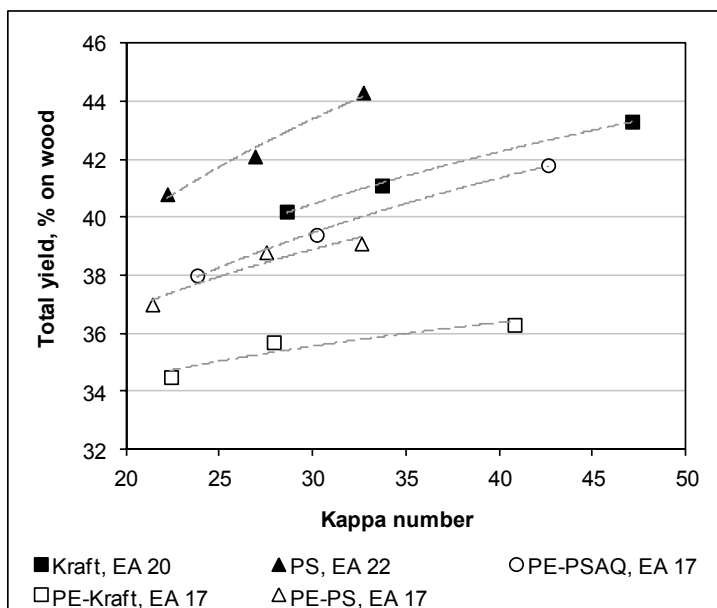
Figure 6 Total yield of Siberian larch laboratory kraft pulp as a function of kappa number. Different kraft cooks and pre-extraction (PE) kraft cooks with polysulfide (PS) and anthraquinone (AQ) were conducted at 167 ℃ to H-factors 850-1650 h. H-factors for pre-extraction PSAQ cooks were 650-1450 h. Pre-extraction temperature of 160 ℃ and time of 60 min were used.

An addition of 0.1% AQ to the pre-extraction PS cook increased the total yield by approximately 0.5% at a kappa number of 30 (PE-PS versus PE-PSAQ). The total yield of the pre-extracted PSAQ pulps was only about 1% lower than that of conventional larch kraft pulp. When the screened yield of pre-extracted PSAQ pulps is compared to conventional kraft pulp the difference is only 0.5%, which is very small considering that 16.6% (**Paper I**) of the wood is removed during pre-extraction. However, it will be very challenging to create 4% PS white liquor in practice.

The results indicated that pre-extracted larch kraft pulps have somewhat higher viscosities than conventional kraft pulps. The addition of PS and AQ to pre-extraction kraft pulping increases the viscosity significantly, over 100 mL/g, at kappa number 30.

At the same pulp kappa number the residual alkali in black liquor was significantly lower for pre-extraction PSAQ cooks compared to other cooks. This shows that PS consumes more alkali, in addition to the sodium hydroxide (NaOH) needed to compensate for the consumption of hydroxyl ions during the preparation of PS liquor. At high temperatures (>130 °C) NaOH is also consumed by formation of thiosulfate from PS, and this may explain the lower residual alkali contents (Dorris, Uloth 1994).

The dry solids content of the black liquors from the pre-extracted cooks was lower than that without pre-extraction consistent with the removal of a substantial amount of wood during pre-extraction and a lower alkali charge used in pulping. PS black liquors had a somewhat higher dry solids content than those without PS because of the sulfur and NaOH addition, as is reflected in the higher content of total sodium (Na) and sulfur (S) in these black liquors. The lower dry solids content of the black liquors after pre-extraction treatment would lead to a significantly lower load for the recovery boiler. This may be an advantage if the recovery boiler is a bottle-neck for increasing capacity. On the other hand, this may be detrimental if additional fuel is needed to meet the energy demand in the mill.

The amount of polysaccharides remaining in the pulps of this study varies from 28% for PE-Kraft pulp to 35% for PS pulp. When comparing the different pulps, it can be seen that pre-extraction leads to the loss of about 1% on wood of glucose for conventional kraft cooking (PE-Kraft versus Kraft). Comparisons between conventional cooking and PS cooking show that the glucose is stabilized and its content increases 2-3% (Kraft versus PS). For pre-extracted PSAQ pulps the glucose yield is increased with 1-2% (Kraft versus PE-PSAQ). It is also clear that pre-extraction leads to xylose loss in the pulp and that this is not affected by the presence of PS or AQ as expected (Pekkala 1986). The presence of PS increases the mannose retention in conventional kraft cooks (PS versus Kraft). Mannose retention with PS is even more pronounced after pre-extraction (PE-PSAQ versus PE-Kraft) with the mannose retention in PE-PSAQ reaching the same level as in regular kraft pulp. In all cases there is only a very small amount of galactose and arabinose remaining in the pulp (based on wood).

Thus the effect of PSAQ kraft pulping after pre-extraction is that the subsequent additional loss of glucose and mannose during kraft pulping is eliminated. The glucose and mannose yields in PE-PSAQ pulps are even higher than in Kraft

pulps. The likely mechanism is that PS and AQ stabilize newly created reducing ends in respectively glucomannan and cellulose. Since PS and AQ have no significant effect on the final content of arabinogalactan in larch pulp, pre-extraction of this hemicellulose is advantageous from the point of view of further utilization of these sugars, minimization of alkali consumption, and minimal impact on pulp yield and properties. The amount of sugars dissolved in the extract after water extraction at 160 °C for 60 min is significant at slightly above 50 g/L (**Paper I**). This may be further increased by reusing the wash water generated during chip washing at the end of the hot water treatment as feed liquor in the extraction unit. Other potential improvements are further optimization of the extraction conditions which keep the removal of arabinogalactan at a high level but reduce the dissolution of especially glucomannan. It is expected that at these conditions the charge of PS can be reduced and mill implementation of this concept becomes even more attractive.

4.5.1   Properties of unbleached pulp

Strength and optical properties of laboratory hand sheets of four different pulps were tested and effects of beating on pulp properties were analyzed (**Table 16**). It can be seen that the beatability of unbleached larch pulp is somewhat lower for the pre-extracted pulps compared to the conventional Kraft and PS pulps. The apparent density of the pre-extracted PSAQ pulp sheets is higher than that of conventional kraft pulp. The tensile strength of the beaten pre-extracted PSAQ pulp is comparable to conventional kraft pulp. However, tear and zero-span strengths and optical properties of the pre-extracted PSAQ pulp are slightly lower

Table 16 Paper technical properties of Siberian larch unbleached laboratory pulps with kappa number 26-30. Pulps were beaten in a PFI mill for 1000 revolutions.

Paper tech. properties (PFI mill 1000 revs.)	Kraft (K29)	PS	PE Kraft	PE PSAQ
SR	14.0	14.2	13.2	13.7
Density, kg/m^3	504	511	487	551
Tensile, Nm/g	50.5	54.0	33.7	50.4
Tear, Nm^2/kg	19.2	17.2	21.8	17.2
Zero span, Nm/g	167	163	160	163
ISO-brightness, %	18.9	18.4	21.4	16.6

than that of conventional kraft pulp. These results must be verified after bleaching the pulps to full brightness for more definite conclusions regarding the final paper properties.

4.6   PE-PSAQ pulping: washing and PS charge (Paper III)

The chips were pre-extracted under optimum conditions (150 °C, 90 min), i.e. minimal removal of xylan and glucomannan at highest arabinoglucan removal, and then cooked with both polysulfide (PS) and anthraquinone (AQ). Pre-extraction (PE) at 150 °C for 90 min removes 11.2% (**Paper III**) sugars from the wood chips. Three different levels of washing of the extracted chips were tested (no, mild, and extensive), as well as three different PS charges during the cook (0.5%, 1.0%, and 2.0%). The basic cooking results from the trials conducted within this study are presented in **Table 17**. The kappa numbers of the pulps were about 26, except for the unwashed PE-PSAQ pulps which have kappa numbers around 30. A higher alkali charge (23% compared to 20%) was used for

Table 17 Conditions, pulp and black liquor properties for PE-PSAQ pulping of Siberian larch (Pre-extraction: L/W 3.5, 150 °C for 90 min, heat-up time 60 min; Washing: no, mild or extensive; Cooking: L/W 3.5, heat-up time 60 min, 167 °C).

	PE-PSAQ								
Washing	No	No	No	Mild	Mild	Mild	Ext	Ext	Ext
Cooking									
H-factor, h	1250	1250	1250	1250	1250	1250	1250	1250	1250
Effective alkali charge, %	20	20	20	20	20	20	20	20	20
Polysulfide charge, %	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Anthraquinone charge, %	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sulfidity of white liquor, %	38.1	38.1	38.1	38.0	38.0	38.0	38.0	38.0	38.1
Sulfidity of PS liquor, %	38.6	39.8	42.1	38.1	39.5	42.0	38.6	39.9	42.1
NaOH addition, %	0.1	0.4	1.2	0.3	0.7	1.4	0.4	0.8	1.2
Pulp									
Yield, %	36.9	37.3	38.3	37.2	36.8	38.4	37.2	37.2	38.1
Reject, %	0.2	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1
Kappa number	29.8	31.0	30.9	26.3	25.5	25.9	25.0	25.4	25.5
Viscosity, mL/g	1128	1129	1173	1023	1024	1005	1039	1029	1053
Black liquor									
pH	13.2	13.2	13.1	13.4	13.4	13.3	13.3	13.3	13.2
Residual alkali, g NaOH/L	7.0	7.7	6.3	8.8	9.6	6.8	9.8	10.2	6.7

the kraft cook in order to reach the kappa number around 26. The yield for the latter control kraft cook of about 40% is 2 % higher than the mildly washed PE-PSAQ treatment at 2% PS charge and both pulps having a kappa number of about 26. The viscosity was higher for the PE-PSAQ pulps. The residual alkali was higher than 6 g NaOH/L in all black liquor samples, which means that there was enough alkali in all cooks.

4.6.1   Influence of washing and PS charge

Total pulp yields obtained for the PE-PSAQ cooks are presented as a function of kappa number in **Figure** 7. Washing reduces the kappa number from 30 to 26. The mild wash is sufficient to obtain this effect. PS charges of 0.5% and 1.0% give yields of about 37%, whereas the yield increases to above 38% with a PS charge of 2%. If the unwashed PE-PSAQ pulps had been cooked to kappa number 26, more alkali would have been consumed and the yield would have been lower.
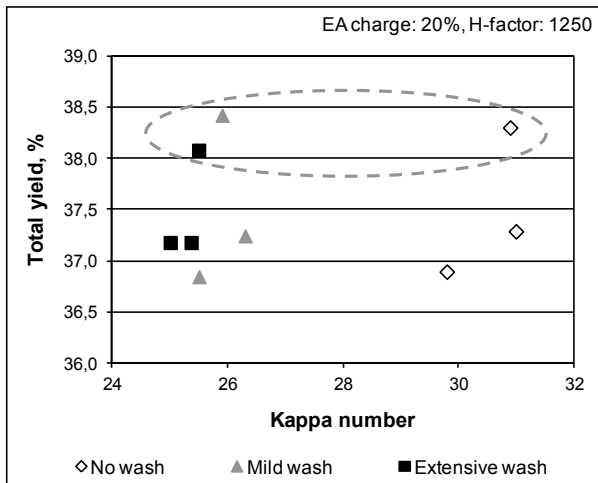
Figure 7 Total pulp yield versus kappa number for PE-PSAQ pulping of Siberian larch with different degree of washing.

In **Figure 8** the viscosity is plotted against PS charge. No washing of extracted chips resulted in about 100 mL/g higher viscosity, but these pulps also had a higher kappa number. There was no significant difference between the final viscosity and kappa numbers of the pulps produced after a mild or extensive wash. The PS charge had no influence on the viscosity.
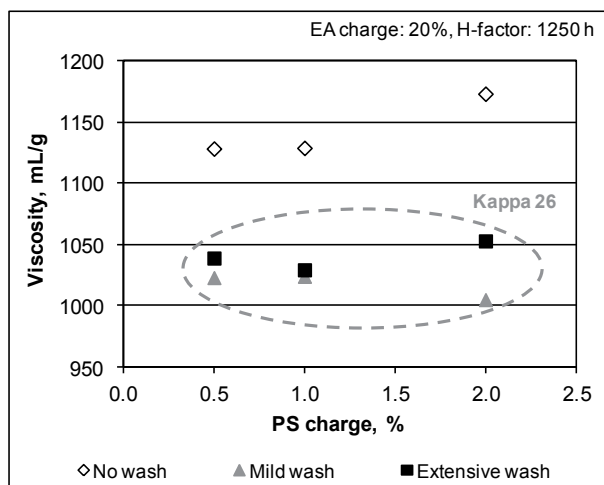
Figure 8 Viscosity of pulp versus PS charge for PE-PSAQ pulping of Siberian larch with different degree of washing.

More alkali was consumed with no washing and when the PS charge was 2.0%. When the extracted chips were not washed, the dissolved sugars remained within the extracted wood and the pH of the wood for pulping was about 4. The dissolved sugars remaining in the pre-extracted chips and the acidity consumed a significant amount of the cooking chemicals, while PS decomposed to thiosulfate. Washing of extracted chips removes the dissolved sugars and acetyl groups/acetic acid from the chips, resulting in decreased consumption of cooking chemicals.

Based on these results the optimal and most practical conditions would be a process including pre-extraction at 150 °C for 90 min, followed by a mild wash and PSAQ pulping at a PS charge of 2%.

The carbohydrate compositions of the different pulps based on original wood are presented in **Figure 9**. The PE-PSAQ pulps subjected after PE to a mild or an extensive washing are here compared to the control kraft pulp, because they had essentially the same kappa number as the control (kappa 26). The no-wash pulps had kappa numbers around 30, and are therefore more difficult to compare. It can be seen that these PSAQ pulps had about 2 to 3% on wood less glucan, 0 to 1% on wood less mannan, and about 1% on wood less xylan than the control kraft pulp. The amount of galactan was very small, and no arabinan could be detected in all cases, including the control kraft pulp. This shows that it is advantageous to remove as much of the arabinogalactan during pre-extraction, because it will dissolve anyway during kraft cooking in the black liquor. The lower glucan

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content in the final pre-extracted kraft pulp is not due to removal of glucose during pre-extraction. This means that the extra cellulose loss during cooking is mostly responsible for the pulp yield loss of the PE-PSAQ pulps.
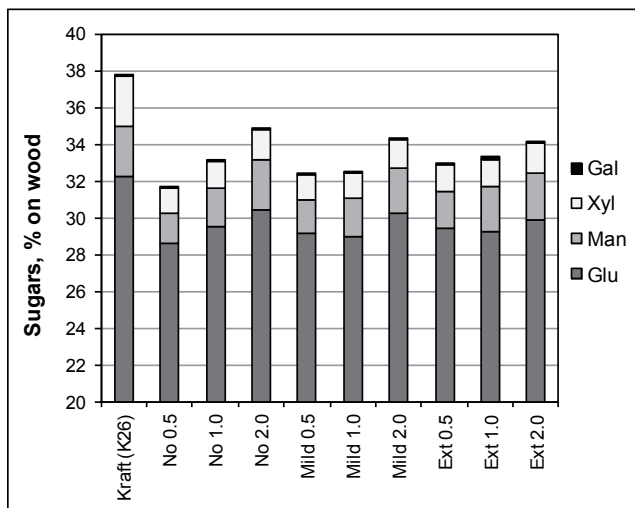

Figure 9 Carbohydrates in kraft pulp and PE-PSAQ pulps. The kappa number is about 26 for all pulps. The pre-extraction was performed at 150 °C for 90 min. Three different levels of washing (no, mild, and extensive), and three different PS charges (0.5, 1.0, and 2.0%) were tested.

Among the PE-PSAQ pulps it can be seen that a higher PS charge preserved glucan and mannan, which was also claimed in the literature (Pekkala 1986; Luthe, Berry 2005; Jiang 1995; van Heiningen et al. 2004). The xylan and galactan contents were similar in all PE-PSAQ pulps. The decrease in glucan content in the PE-PSAQ pulps compared to the kraft pulp was most likely due hydrolytic cleavage of cellulose during PE treatment. This leads to a lower DP of cellulose and new reducing ends, which contribute to additional peeling during subsequent PSAQ cooking. No significant amount of cellulose was dissolved as glucan during PE treatment because the degree of polymerization (DP) was too high for dissolution. More cellulose will be retained by increasing the AQ charge (van Heiningen et al. 2004) or by adding sodium borohydride, as was done by Yoon et al. (Yoon et al. 2010). The lignin and extractives contents for both kraft pulp and PE-PSAQ pulps were about 1.3% on wood and 0.1% on wood, respectively.

The characteristics of the kraft control and two PE-PSAQ black liquors obtained after the mild washing step are presented in **Table 18**. The dry solids contents of the two PE-PSAQ black liquors are lower than the control because of the 3% lower effective alkali charge. The similar or higher heating values of the PE-PSAQ black liquors compared to the control implies that the amount of organics dissolved during cooking was similarly decreased as the inorganics were reduced in charge. The slightly higher heating value for the Mild 0.5 sample was due to the slightly higher wood dissolution, resulting in a lower pulp yield than for the Mild 2.0 sample. Because of the very similar organics to inorganics ratio, it is unlikely that the burning properties of black liquor will be affected when converting from conventional kraft to the PE-PSAQ process for larch wood.

Table 18 Heating values for three black liquor samples.

	Kraft (K26)	PE-PSAQ	
Wash of extracted chips	-	Mild	Mild
PS charge	-	0.5	2.0
Density, g/cm^3	1.153	1.117	1.117
DM, % on liquor	21.6	18.7	18.7
Ash, % on liquor	0.45	0.46	0.46
Heating value (Hu,p (wf)), MJ/kg	13.9	14.4	13.9

4.6.2 Comparisons with other processes

The pre-extraction PSAQ process with a mild wash and a PS charge of 2% (PE-Mild-PS(2%)AQ process) was compared to kraft, pre-extraction kraft, and pre-extraction PSAQ at 4% PS charge, the latter two performed with extensive washing of the extracted chips (PE-Ext-Kraft and PE-Ext-PS(4%)AQ). In **Figure 10** the total pulp yield of these four processes are shown as function of the kappa number. The PE-Ext-Kraft and PE-Ext-PS(4%)AQ were performed with pre-extraction at 160 °C for 60 min dissolving 16.7% sugars (**Paper I**), while the pre-extraction of the PE-Mild-PS(2%)AQ was performed at 150 °C for 90 min dissolving 11.2% sugars (**Paper III**).

From **Figure 10** it can be seen that removing carbohydrates through PE at a level of 16.7% (**Paper I**) on wood reduced the pulp yield by 5% (40.2% for Kraft minus 35.2% for PE-Kraft) at kappa number 26. This loss was significant, but still smaller than the 7% yield loss obtained for Scots pine at about 7% PE sugars

removal (Kautto et al. 2010), showing that without stabilization of the carbohydrates the PE sugar yield minus pulp yield loss is 11.7% (=16.7%-5%) for larch compared to essentially zero for Scots pine. The latter has also been found for loblolly pine and hardwoods, as was reviewed earlier. The obvious explanation is that for larch a large amount of arabinogalactan can be extracted before it is almost fully removed during kraft pulping, while for other softwoods as well as for hardwoods the removal of glucomannan and xylan in significant amounts also leads to significant additional peeling of these hemicelluloses during pulping and thus a large yield loss.
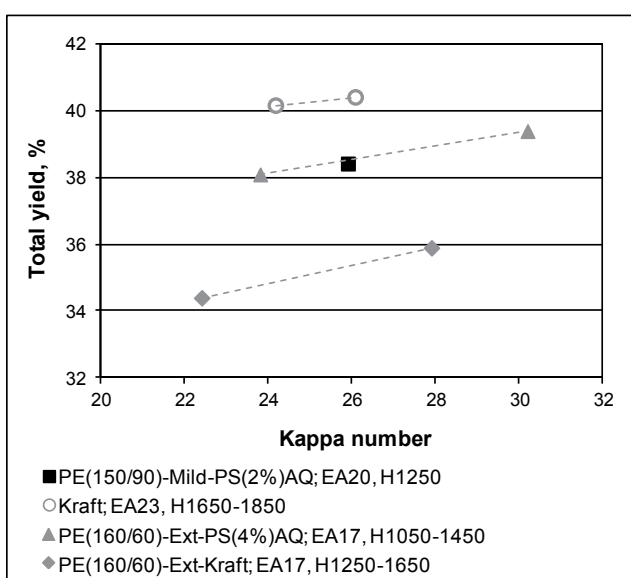
Figure 10 Total pulp yield versus kappa number. The PE-Mild-PS(2%)AQ pulp is compared with other pulps.

By using 2% PS and 0.1% AQ the yield loss was reduced to 2% (40.2% for Kraft minus 38.2% for PE-Mild-PS(2%)AQ) at a PE sugar yield of 11.2% (**Paper III**). In comparison, Yoon et al. (2011) also obtained 2% pulp yield loss for loblolly pine at 10% PE sugars, but at an order of magnitude higher PS charge of 15 to 20% with also 0.1% AQ. The explanation for the higher efficiency in yield retention of PS in the present experiments is that milder extraction conditions are used with larch as feedstock (because of the higher solubility of arabinogalactan) leading to fewer new reducing ends in the residual hemicelluloses as well as

cellulose and thus requiring less oxidative stabilization by PS and AQ. Most of the 2% pulp weight loss was due to cellulose loss (**Figure 9**).

It is interesting to note that Yoon et al. (Yoon et al. 2010) were able to fully recover all cellulose and pulp yield by treatment of loblolly pine PE pulp with 1% sodium borohydride ($NaBH_4$) before kraft-AQ pulping. This suggests that a reductive treatment is most effective to stabilize cellulose. Unfortunately, a more economical reductive treatment is still lacking.

The PE(150/90)-Mild-PS(2%)AQ process can be judged to be better than the PE(160/60)-Ext-PS(4%)AQ, because the former also achieves a 2% lower pulp yield but with half the PS charge. Other beneficial aspects of the PE-Mild-PSAQ process compared to the kraft process are lower alkali charge (20% versus 23%) and 600 h lower H-factor (1250 h versus 1850 h). Negative economic aspects of the optimal PE-Mild-PS(2%)AQ process besides the 2% pulp yield loss are additional operating cost (e.g. PS and AQ) and capital cost (PE vessel and extract processing equipment). By combining the extract and the wash water streams, the sugar yield can be further increased.

4.7   Bleachability and paper properties (Paper IV)

The results from the bleaching experiments and the testing of paper properties of a kraft pulp and two different PE-PSAQ pulps are discussed here. The following three larch pulps with kappa numbers around 26 were bleached and tested: 1) Kraft, 2) PE-Mild-PS(0.5%)AQ (here called PS0.5), and 3) PE-Mild-PS(2%)AQ (here called PS2.0). Here, the PE was performed at 150 °C and 90 min, dissolving 11.2% (**Paper III**) sugars of wood. The decreasing development of the kappa number during bleaching is presented in **Figure 11**, where also the ISO brightness after the D1 stage is recorded. In general, the PE-PSAQ pulps are somewhat easier to bleach. During the oxygen delignification the decrease in kappa number is about 7 units for the kraft pulp, while about 9 units for the PE-PSAQ pulps. In the following bleaching stages the decreasing trend of the kappa number is very similar. The brightness is higher for the PE-PSAQ pulps (77.7 and 76.2) than for the kraft pulp (71.5). No residual chlorine was detected after the D0 stage, after the other bleaching stages only small amounts of residual chemicals could be determined. The pH values after the different bleaching stages are presented in **Table 19**. All pH values are at the expected levels.
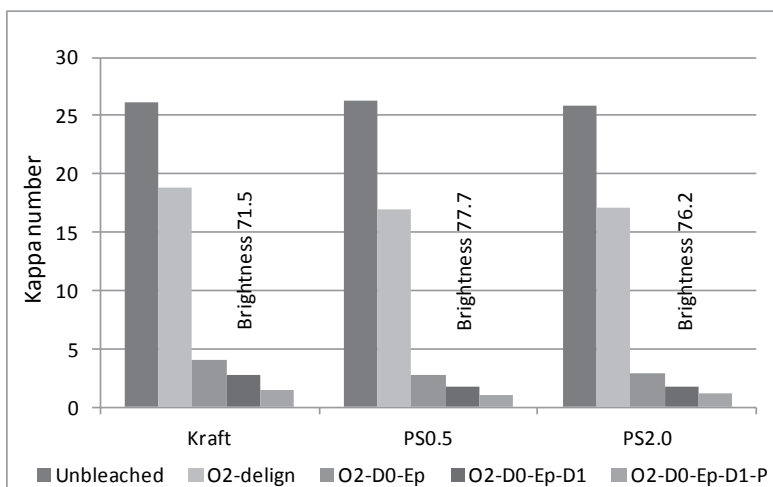
Figure 11 Development of kappa number during bleaching and brightness after D1 stage for three different pulps i.e. kraft, PE-Mild-PS(0.5%)AQ (here called PS0.5), and PE-Mild-PS(2%)AQ (here called PS2.0).

Table 19 pH after different bleaching stages for three different pulps i.e. kraft, PE-Mild-PS(0.5%)AQ (here called PS0.5), and PE-Mild-PS(2%)AQ (here called PS2.0).

End pH	Kraft	PS0.5	PS2.0
O2	10.4	10.5	10.4
O2-D0	2.7	2.4	2.4
O2-D0-Ep	10.0	9.9	9.7
O2-D0-Ep-D1	3.3	3.3	3.9
O2-D0-Ep-D1-P	12.3	12.5	12.6

The brightness of unbleached larch kraft pulp is lower than that of pine and spruce kraft pulp (Nevalainen, Hosia 1969b). Despite of this, the final brightness after bleaching (CEHDED) is almost equal for Siberian larch and Scots pine (Hakkila et al. 1972). This shows that larch pulp is easy to bleach. The brightness reversion is greater for larch pulps compared to pine pulp, but the bleaching yield loss is on the same level for both pulps (Hakkila et al. 1972).

The pulp and paper characteristics of the pulps and paper sheets from this study are presented in **Table 20**, where also a spruce pulp from the literature is presented as a reference (Lindholm 1999). The fiber properties are very similar for all three larch pulps. Somewhat lower SR values, which indicate better water removal, can be pointed out for the PE-PSAQ pulps. The paper properties of the two larch PE-PSAQ laboratory sheets are generally very similar, while the larch

kraft paper slightly differs from the papers of the pre-extracted pulps. The basic sheet properties are similar for all larch papers. Regarding the strength properties, however, there is a significant difference. The PE-PSAQ papers have lower tensile strength and higher tear strength compared to conventional larch kraft paper. The optical properties are all somewhat better for the PE-PSAQ papers. The PE-PSAQ pulps reached higher ISO brightness than the kraft pulp, because of better bleachability of the PE-PSAQ pulps. Also the opacity and the light scattering were higher for the PE-PSAQ pulps. The roughness and the air permeability were both higher for the PE-PSAQ pulps, which can be explained by the lower content of hemicelluloses. Hemicelluloses are removed from the PE-PSAQ pulps during the pre-extraction, which leads to a more porous paper.

Table 20 Pulp and paper properties of three bleached laboratory larch pulps and a spruce pulp from the literature (Lindholm 1999).

Pulp and paper properties			Larch			Spruce (Kraft)
			Kraft	PS0.5	PS2.0	Lindholm 1999
Pulp & fiber	Kappa number		1.5	1.1	1.2	-
	Fiber length (L(l))	mm	2.55	2.48	2.43	2.29
	Coarseness	mg/m	0.202	0.212	0.219	0.185
	Fiber width	µm	29.3	29.0	29.0	-
	Zero span (dry) *)	Nm/g	144	153	146	107**)
	SR *)		18.9	15.3	16.3	22.4
General	Basis weight	g/m2	63.1	62.6	63.2	-
	Density	kg/m3	580	532	573	719
	Bulk	m3/kg	6.9	7.4	7.0	-
Strength	Tensile	Nm/g	64.0	44.2	50.9	70.0
	Tear	mN	15.8	20.4	18.4	17.6
Optical	ISO brigthness	%	77.4	81.6	80.7	88.5
	Opacity	%	62.7	66.2	65.1	70.0
	Light scattering	m2/kg	20.5	24.6	22.8	-
	Absorption	m2/kg	0.18	0.14	0.15	-
Surface	Roughness	mL/min	1945	2244	1844	-
	Air permeability	mL/min	1812	3383	2549	-

*) beaten pulp, **) w et

Comparisons between the PS0.5 pulp and the PS2.0 pulp describe the influence of the PS charge on the pulp and paper properties. The fiber properties are similar, except that the zero span is somewhat higher and the SR value lower for

the PS0.5 pulp (**Table 20**). When comparing the paper properties of the PS0.5 pulp and the PS2.0 pulp, the PS2.0 pulp is closer to the properties of the kraft pulp. The PS0.5 pulp is more porous than the PS2.0 pulp, which is a result from the higher glucomannan content than in the PS0.5 pulp.

Comparisons with other studies allow a more general evaluation of the pulp and paper properties of the present larch pulps. The spruce pulp presented in **Table 20** is a laboratory kraft pulp beaten in the same way as the larch pulps of this study (PFI, 2000 revolutions) The dry zero span of the larch pulps is higher than the wet zero span of the spruce pulp, which indicates that the individual fibers in the larch pulps are stronger because there is no big difference between the dry and wet zero span. The SR values are lower for the larch pulp than for the spruce pulp, especially for the PE-PSAQ pulps. The larch pulp fibers are somewhat longer than the spruce pulp fibres. Lower coarseness gives higher tensile strength (Conclaves 2001). The larch pulps have higher coarseness than the spruce pulp, therefore the spruce pulp has a higher tensile strength than the larch kraft pulp. The PE-PSAQ papers have significantly lower tensile strength, while their tear strength is higher than that of spruce kraft paper. The poor tensile strength of the larch PE-PSAQ papers can be improved by further beating the pulp. Beating affects tear strength and SR values of paper negatively. Since these properties are both better for the PE-PSAQ pulps/papers, further beating is possible. This would probably make the PE-PSAQ papers strength-wise as good as the larch kraft or the spruce kraft paper. The density is higher for the spruce paper than for the larch papers, as are also the ISO-brightness and the opacity.

In the study by Nevalainen and Hosia larch was also shown to have a lower sheet density in the case of unbleached kraft pulps of Siberian larch, Scots pine and Norway spruce (Nevalainen, Hosia 1969b). The lower sheet density of larch unbleached pulp compared to Norway spruce was also observed by Hatton et al. (Hatton et al. 1996). This is probably because of higher fiber coarseness of larch pulps. The larch pulps in the study by Hakkila showed somewhat better strength properties, especially tensile strength, than the larch pulps of this study (tensile 66-75 Nm/g and tear 19-20 nNm²/g at brightness 66-86% and SR 20) (Hakkila et al. 1972). The bleaching sequences in Hakkila's experiments were different from the once used in this study, which perhaps can partly explain these differences. For unbleached pulps the tensile strength was shown to be lower compared to the pine and spruce pulps beaten to the same level, while the tear strength was

significantly higher (Nevalainen, Hosia 1969b). The good tear strength of larch is due to its long fibers and thick-walled latewood fibers. Increasing tree age affects the strength properties by decreasing tensile strength and by increasing tear strength (Hakkila et al. 1972). Industrial ECF and TCF bleached pulp of Scots pine with tensile strength of 50-70 Nm/g had tear strength of 15-20 nNm²/g (Laine 1997). Thus the strength properties of the larch pulps of this study are within the same range as the industrial pine kraft pulps.

The results from this study fit logically into what is generally known about the influences of hemicelluloses removal on paper properties and characteristics. Fewer hemicelluloses leads to less fiber swelling and lower interfiber bonding. This means that the paper will have lower density, higher porosity, lower tensile strength, higher tear strength and better optical properties. Because of the long and strong fibers that larch pulp has, it would be especially suitable for paper with good strength properties i.e. packaging papers and boards and also as reinforcement pulp. There are small variances in the strength properties between the PE-PSAQ pulps and other softwood pulps, but generally the PE-PSAQ pulps could be used for similar applications as other softwoods i.e. pine or spruce.

4.8 Fermentation of larch extract (Paper II, IV)

Two larch extracts produced at different pre-extraction temperatures (120 °C and 160 °C) were fermented and two different hydrolysis methods were studied, i.e. acid hydrolysis (AH) and simultaneous enzymatic hydrolysis and fermentation (SSF). The fermentation results are presented in **Figure 12**, in terms of consumption of monosugars and production of lactic acid. The fermentation of the acid hydrolyzed extracts follows the same pattern as in earlier fermentation studies on larch extract (Walton et al. 2010). First, glucose and mannose are consumed, and, after a lag phase of about 10 hours, the consumption of xylose, arabinose and galactose occurs. The initial lag phase may be due to inhibitory substances such as acetic acid, furfural, HMF and lignin derived phenolics. All monosugars are consumed during the fermentation with *Bacillus coagulans* MXL-9 after about 80 hours.

In the case of the 160 °C extract about 36 g/L monosugars were converted into about 28 g/L lactic acid. This means a fermentation yield of about 78%. From the 120 °C extract containing about 18 g/L monosugars, 10 g/L lactic acid was
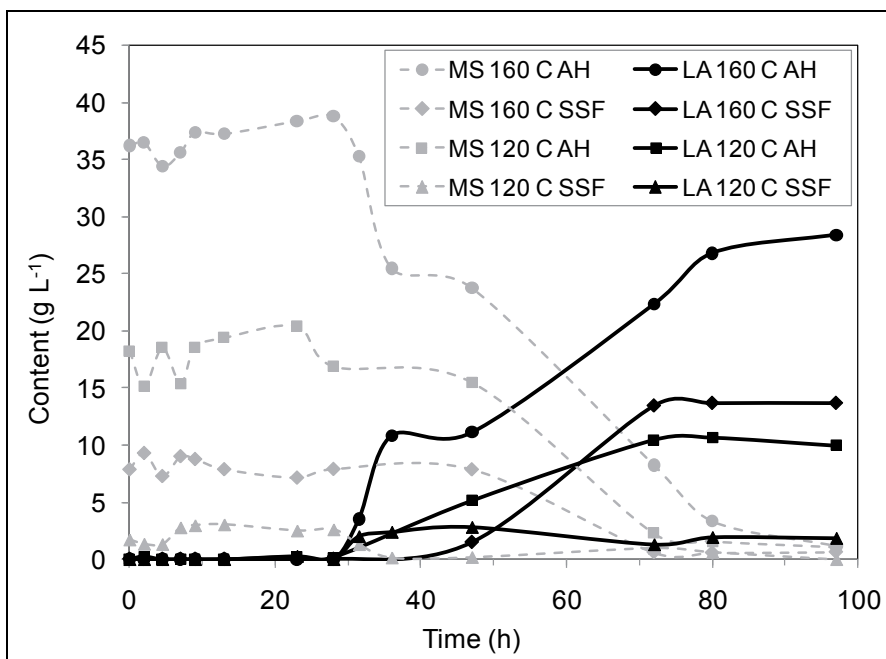
Figure 12 Lactic acid production through fermentation of larch (*Larix sibirica*) extracts produced at 120 °C and 160 °C. Two different hydrolysis methods were tested; acid hydrolysis prior to fermentation (AH) and simultaneous enzymatic hydrolysis and fermentation (SSF). The consumption of monosugars (MS) and production of lactic acid (LA) are presented as a function of fermentation time.

produced, resulting in a fermentation yield of about 56%. The SSF treatment did not give as good results as separate acid hydrolysis followed by fermentation. The amount of lactic acid produced through fermentation combined with enzymatic hydrolysis was significantly lower than that for the acid hydrolysis followed by fermentation. The amount of lactic acid produced in the enzymatic fermentation cases were 14 g/L and 2 g/L for 160 °C and 120 °C, respectively. Earlier studies show that fermentation combined with enzymatic hydrolysis work well on hardwood extract, containing mostly xylan (Walton 2009). Enzymes with different activities more suited to the specific types of bonds found in the larch extract would need to be found for SSF to be successful in the production of lactic acid. During the fermentation also some by- products were formed; formic acid (3.0 g/L), acetic acid (2.8 g/L) and ethanol (0.5 g/L). The maximum by-product production is mentioned in brackets and occurred in the fermentation of the 160 °C extract, with both the acidic and the enzymatic treatment.

Different *Clostridium* and *Lactobacillus* strains were tested in order to ferment sugars of hydrolyzed larch extract (HLE) into valuable substances like lactic, acetic and butyric acids, ethanol and butanol. The results from the fermentation are presented in **Table 21**. The initial sugar content of the extracts was 35-43 g/L, and after fermentation the sugar content was 15-38 g/L. Generally, the hexoses were more actively utilized and galactose was rather inefficiently consumed by all these bacteria strains.

Of the *Lactobacillus* strains *L. plantarum* DSM 20314 was the most efficient to ferment the larch extract. It actively utilized hexoses (glucose, galactose, and mannose), fermented arabinose less efficiently, and was not able to metabolize xylose. The two *L. brevis* strains and *B. coagulans* VKPM B-10468 revealed similar fermentation profiles producing lactate, acetate and ethanol. Arabinose was almost completely utilized for 72 h fermentation by all three strains. Mannose was not consumed at all by *L. brevis* strains. Rate of galactose utilization was highest for *B. coagulans* VKPM B-10468 and lowest for *L. brevis* 5563 strain. It should be noted that the end product profile of heterofermentative *B. coagulans* VKPM B-10468 strain differs from *B. coagulans* MXL-9 (**Paper II**) producing mainly lactate.

All the *Clostridium* strains showed weaker fermentation results. The sole product of *C. acetobutylicum* MSU 6 was lactate. *C. acetobutylicum* MSU 7 weakly fermented sugars of hydrolyzed larch extract and produced acetate and butyrate in trace amounts. *C. acetobutylicum* VKPM B-4786 produced lactate, acetate, ethanol, butanol, and butyrate. *C. saccharobutylicum* VKPM B-10183 produced butyrate and butanol. *Clostridium* strains preferred glucose and mannose over galactose and arabinose.

Lactate was produced by *L. plantarum* DSM 20314, *L. brevis* ATCC367, *L. brevis* ATCC8287, *B. coagulans* VKPM B-10468 and *C. acetobutylicum* MSU 6. The highest fermentation yield for 72 h cultivation was obtained by producing lactate with *L. plantarum* (1.7% on wood). Acetate was produced by all strains tested in this study. Ethanol was produced by two *L. brevis* strains, *B. coagulans* VKPM B-10468, and *C. acetobutylicum* VKPM B-4786. Butanol was actually produced only by *C. saccharobutylicum* VKPM B-10183. Butyrate was produced by *C. acetobutylicum* VKPM B-4786 and *C. saccharobutylicum* VKPM B-10183 strains.

The fermentation experiments with *B. coagulans* MXL-9 gave the most attractive results (**Paper II**).

Table 21 Results from fermentation of larch extract for 72 h of cultivation.

	L. brevis ATCC367	L. brevis ATCC8287	L. plantarum DSM 20314	B. coagulans VKPM B-10468	C. acetobutylicum MSU 6	C. Acetobutylicum MSU 7	C. acetobutylicum VKPM B-4786	C. saccharobutylicum VKPM B-10183
Initial sugar content, g/L								
Total sugar	**39.3**	**38.8**	**40.5**	**42.8**	**34.4**	**35.3**	**36.1**	**35.1**
Arabinose	6.6	6.5	6.8	7.2	5.8	5.9	6.1	5.9
Galactose	26.1	25.7	26.9	28.4	22.8	23.4	24	23.3
Glucose	1.3	1.3	1.4	1.4	1.2	1.2	1.2	1.2
Xylose	2.0	2.0	2.0	2.2	1.7	1.8	1.8	1.8
Mannose	3.3	3.3	3.4	3.6	2.9	3.0	3.0	2.9
Sugar content after 72 h of cultivation, g/L								
Total sugar	**25.5**	**18.2**	**14.9**	**16.2**	**25.1**	**37.9**	**27.7**	**24.7**
Arabinose	0.5	0.3	3.5	0.3	6.8	8.2	4.3	3.8
Galactose	20.5	14.6	8.7	13	16.5	24.3	22.2	19.9
Glucose	0.0	0.0	0.0	0.0	0.0	1.1	0.0	0.0
Xylose	1.2	0.0	2.0	0.0	1.8	2.0	1.2	1.0
Mannose	3.3	3.3	0.7	2.9	0.0	2.3	0.0	0.0
Total sugar utilized	**13.7**	**20.6**	**25.6**	**26.6**	**nd**	**nd**	**8.4**	**10.4**
Pentose utilized	6.9	8.2	3.3	9.1	nd	nd	2.4	2.9
Hexose utilized	6.8	12.4	22.3	17.5	10.4	nd	6.0	7.5
Fermentation products, % on wood								
Total products	**1.4**	**2.3**	**2.7**	**2.2**	**1.6**	**0.7**	**1.4**	**1.0**
Lactate	0.5	0.9	1.7	0.8	1.0	0.0	0.0	0.0
Acetate	0.7	1.1	0.9	1.0	0.6	0.6	0.8	0.4
Ethanol	0.1	0.3	0.0	0.4	0.0	0.0	0.0	0.0
Butanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
Butyrate	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.3

nd - Sugar concentarations cannot be determined because of hemicellulase activity of the strains.

4.9   The designed larch biorefinery process (Paper V)

A realistic and practical larch biorefinery process was developed. In this larch biorefinery concept hemicelluloses are removed with water in a pre-extraction (PE) step before kraft pulping with polysulfide (PS) and anthraquinone (AQ). The wood fibers become bleached softwood pulp for i.e. packaging paper, and the hemicellulose-rich extract is fermented to lactic acid. **Figure 13** presents a kraft pulp production unit, whereas a combined kraft pulp and lactic acid production process for larch wood (PE-PSAQ process) is presented in **Figure 14**.

This kind of larch biorefinery gains additional revenue from the lactic acid production. The combined pulp and lactic acid production site could be a green field mill, but preferably a pre-extraction stage and lactic acid production unit could also be added to an existing pulp mill. The PE-PSAQ process was planned using practical conditions and equipment available on the market. This larch biorefinery process is mainly developed based on the earlier described experiments (**Paper II; Paper III; Paper IV**). In the proposed PE-PSAQ process the PS liquor is, however, not prepared by dissolving elemental sulfur as was done in the laboratory experiments, but in a MOXY reactor (Andritz 2012; Smith, Sanders 1977). Information about the purification of lactic acid has been taken from the literature (Datta 1995; Glassner, Datta 1990; Lee et al. 1998).

Compared to a conventional kraft process, the PE-PSAQ process needs the following additional processing units (grey boxes in **Figure 12**): extraction, washing, hydrolysis, neutralization, fermentation, a MOXY reactor, and a natural gas fired boiler. The additional inputs (grey boxes in **Figure 12**) are steam for pre-extraction of wood, AQ for PSAQ pulping, sulfuric acid (H_2SO_4) for hydrolysis, calcium hydroxide ($Ca(OH)_2$) for neutralization, nutrition for bacteria and potassium hydroxide (KOH) for pH adjustment. The bacteria in the process reproduce themselves, and except during start-up do not need to be purchased. The product in addition to bleached pulp is lactic acid. Gypsum is formed as a by-product from the neutralization step.
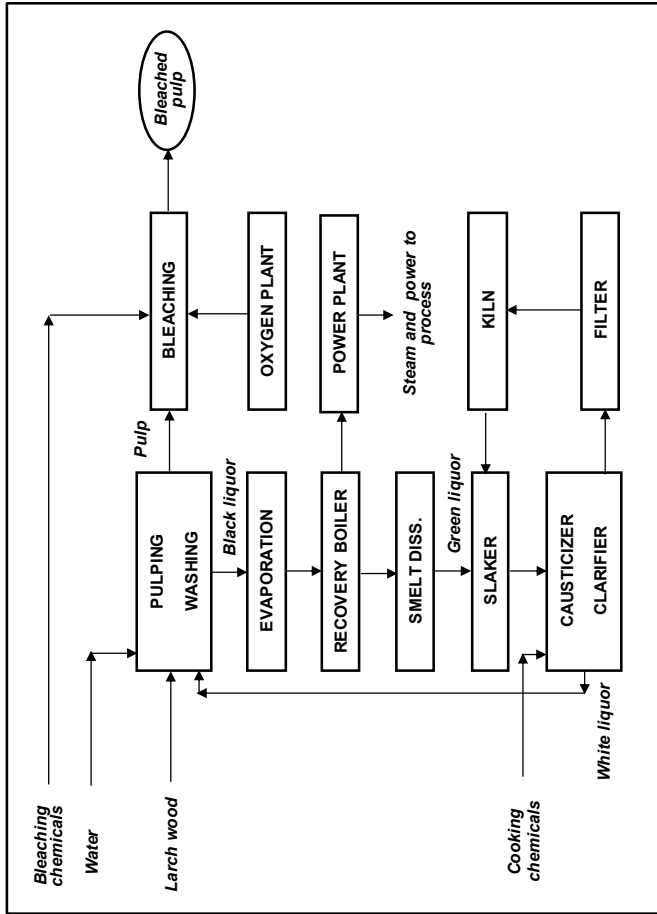
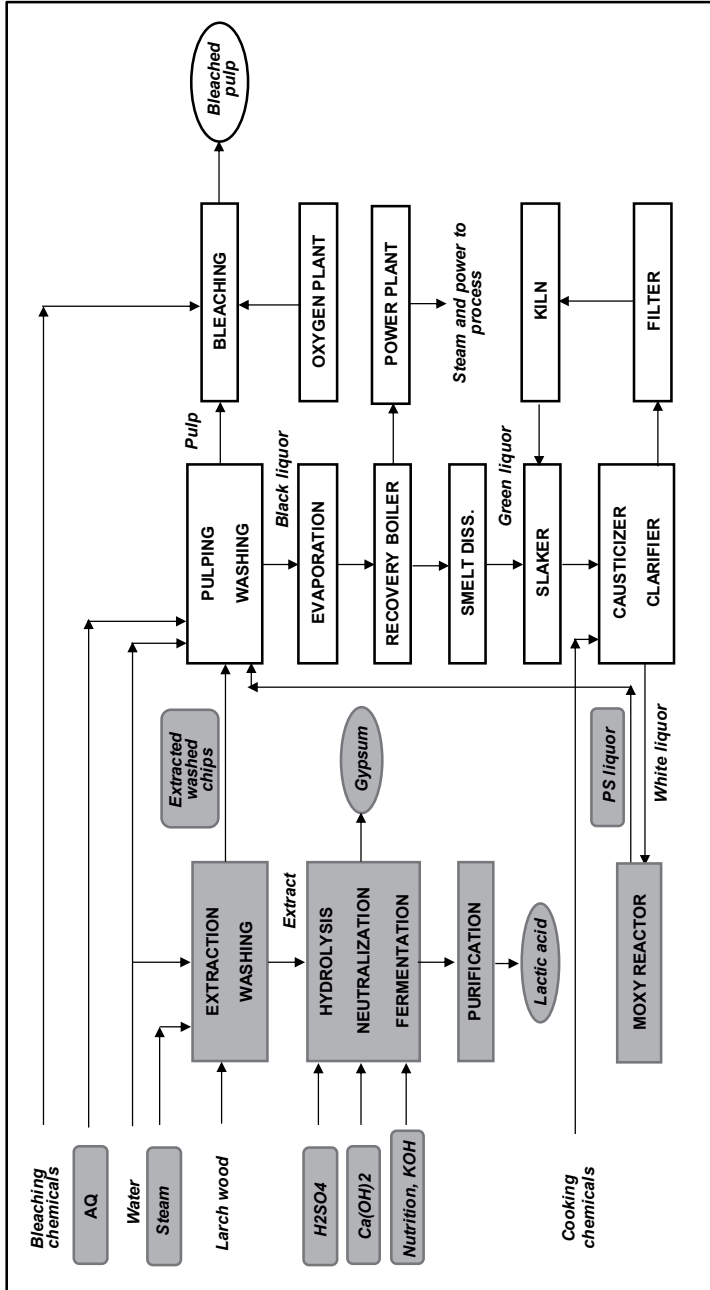**Figure 13** Process flowchart of a kraft pulp production process.

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Figure 14 Process flowchart of a combined kraft pulp and lactic acid production process for larch wood.

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In the PE-PSAQ process the larch wood chips are treated with water in a pre-extraction unit for 90 min. The ideal temperature is about 150 °C, whereby mostly the arabinogalactan dissolves which otherwise would be fully removed during regular kraft pulping, while xylan is mostly retained (**Paper II**). The pre-extracted chips are drained and then mildly washed, in order to remove most of the dissolved sugars from the extracted wood chips (**Paper III**) while minimizing the amount of wash water (dilution factor 2). The drained extract and the wash water from washing the extracted chips are combined.

The pre-extracted and washed chips are cooked with PS liquor, to which also AQ is added, in order to maintain the pulp yield. A PS charge of 2% on wood and an AQ charge of 0.1% of wood is enough to maintain the yield at 2% below the level as kraft pulping (**Paper III**). The pulp is washed and bleached (O-D0-Ep-D1-P). Less bleaching chemicals are needed for the bleaching of the PE-PSAQ pulp, and the PE-PSAQ pulp quality is comparable with other softwood kraft pulp (**Paper IV**). The black liquor, with dry solids content somewhat lower but dry solids heating value the same asthat in kraft pulping (**Paper IV**), is burnt and recovered. A MOXY reactor is used for regenerating the PS liquor (Andritz 2012; Smith, Sanders 1977). Otherwise, the recovery process is the same as in the kraft case.

The combined sugar stream of extract and wash water is acid hydrolyzed, neutralized with slaked lime and then fermented (**Paper II**). The polymeric sugars are hydrolyzed with sulfuric acid into monosugars, in order to be available for the bacteria in the fermentation unit. The solution is neutralized with calcium hydroxide ($Ca(OH)_2$) before fermentation. The neutralization results in formation of gypsum as by-product. During fermentation the bacteria (*Bacillus coagulans* MXL-9) converts the sugars into lactic acid at a high yield.

The lactic acid has to be purified in order to sell it on the market. A two-stage membrane technology was chosen for lactic acid purification in this larch biorefinery (Glassner, Datta 1990; Lee et al. 1998). The purification process contains a desalting electrodialysis, a water-splitting electrodialysis and an ion exchange stage. The lactate salt-containing broth from the fermentation is fed to the first electrodialysis step (desalting). There the lactate salt i.e. sodium lactate is recovered and concentrated. Viable bacteria cells are fed back to the fermentation unit. Then the concentrated lactate is fed to the second bipolar electrodialysis step (water-splitting). An aqueous lactic acid solution is formed, and also a base.

The base is recycled back to the fermentation unit. The lactic acid solution is then fed to an ion exchanger unit. First it is treated by a strongly acidic cationic exchange resin and then a weakly basic anionic exchange resin to remove positively and negatively charged impurities producing a highly purified form of lactic acid solution (purity 90-100%). The by-product gypsum ($CaSO_4*2H_2O$) may for example be used as fertilizer or to produce wallboard for construction purposes (Charola et al. 2007; Founie 2003). However, because the market price of crude gypsum is very low i.e. 5 €/t (Founie 2003) the revenue accounting for transport would be negative. Therefore, the gypsum is landfilled near the site in this study.

4.10 Technical and economic aspects (Paper V)

Two slightly different larch biorefinery processes are compared to a larch kraft process. The following three cases were studied; 1) a larch kraft process, 2) a PE-

Table 22 Assumptions for the evaluation.

Assumptions
General
Planned location: Siberia in Russia, in the area of the Yenisei river
Wood raw-material: Larix sibirica Lebed.
General grid is close to the mill
Other labor needed: 50 persons
Operating time: 350 days/year (8400 h)
Currency: € (1 € ~ 1.30 US$)
Pulp mill
Production capacity: 400,000 t pulp/year (about 1000 t/day)
Consistency of produced bleached pulp: 90 %
No external energy is needed for pulp mill
Labor needed for pulp mill: 400 persons
Pre-extraction and lactic acid (LA) production
Addition of lactic acid production to a greenfield or existing pulp mill
Additional process units: pre-extraction, washing, hydrolysis, neutralization,
fermentation, purification, MOXY reactor, natural gas boiler
External energy in form of natural gas is needed for the lactic acid production
The bacteria are re-producing in fermentation
Costs for fermentation chemicals: 100 €/t
Consumption and cost for LA purification chemicals have not been considered
The produced by-product gypsum is left on site
Labor needed for lactic acid production: 50 persons
Extra costs for waste water treatment of effluent from lactic acid recovery
process were not included

PSAQ process with PS charge 0.5% on wood, and 3) a PE-PSAQ process with PS charge 2.0% on wood. The assumptions used in the evaluations are summarized in **Table 22**.

4.10.1 Technical evaluation

The technical characteristics of the three process cases are presented in **Table 23**. Basic information i.e. capacity, charges and yields are mentioned in order to thoroughly describe the different processes. Values for chemical and energy consumption have been taken from the WinGEMS simulation results.

Case II has the highest wood demand, due to lowest pulp yield. As a result of pre-extraction a lower amount of carbohydrates is going into the pulping step with the extracted wood chips in Case II and III. Therefore, less alkali and a lower H-factor can be used in the PE-processes (**Paper III**). The PE-pulps are easier to bleach (**Paper IV**), which results in lower consumption of bleaching chemicals in Case II and III. Somewhat more lactic acid is produced in Case II compared to Case III, because the wood demand in Case II is larger. Therefore, the chemical consumption of the lactic acid production is also somewhat larger for Case II. Based on own experiments, the amount of gypsum formed was estimated to be about 75% of the lactic acid production.

External energy (about 20%) is needed for the pre-extraction step in Case II and III, while the kraft process is self-sufficient regarding energy. Steam is produced in the process. A part of the produced steam is also consumed by the process, and the remaining steam is converted to power. The power is used in the process, and the net power of the three integrated cases is very close to zero.

4.10.2 Market prices

Market and mill gate prices for the products are presented in **Table 24**. During the last 10 years the market price for pulp has fluctuated between 500 and 700 €/t pulp (Indexmundi 2013). In 2009 the price dropped briefly to about 400 €/t pulp, but then immediately increased again. In April 2013 the market price for Northern Soft Wood Bleached Kraft (NSWBK) pulp was 650 €/t (Paperage 2013).

Table 23 Process information from experiments and simulation results.

Process information		Case I Kraft	Case II PE-PS(0.5)AQ	Case III PE-PS(2.0)AQ
Capacity of bleached pulp (dry)	t/year	400,000	400,000	400,000
Pre-extraction (PE) and washing				
Wood demand (dry)	t/year	1,108,499	1,221,960	1,183,548
Wood demand (wet)	t/year	2,216,997	2,443,920	2,367,097
Sugar yield	% on wood	-	10.2%	10.2%
Dissolved sugars (100%)	t/year	-	124,640	120,722
Pulp production				
Effective alkali	% on wood as NaOH	23%	20%	20%
Sulfidity	% on wood	37.6%	38.1%	41.9%
H-factor	h	1,650	1,250	1,250
Kappa number		26	26	26
Polysulfide charge	% on wood	-	0.5	2
Anthraquinone charge	% on wood	-	0.1	0.1
Cooking chemical consumption	t/year	20,991	18,429	15,810
NaOH makeup (100%)	t/year	20,991	17,366	14,781
CaCO3 (100%), 30 kg CaCO3/t pulp	t/year	12,000	12,000	12,000
Anthraquinone consumption (100%)	t/year	-	1,063	1,029
Pulp yield	% on wood	40.4%	36.3%	37.5%
Unbleached pulp production (dry)	t/year	448,029	443,593	443,593
Bleaching chemical consumption	t/year			
MgSO4 consumption (1.5%)	t/year	18,325	13,574	13,575
H2SO4 consumption (5%)	t/year	116,500	65,856	65,857
NaOH consumption (4%)	t/year	206,121	206,116	206,117
H2O2 consumption (5%)	t/year	140,246	140,242	140,243
NaCl consumption (100%)	t/year	15,400	13,447	13,447
NaClO3 consumption (100%)	t/year	28,146	24,575	24,575
H2SO4 consumption (100%)	t/year	26,021	22,720	22,721
Bleaching yield	% on unbleched pulp	90.0%	90.9%	90.9%
Bleached pulp production (dry)	t/year	403,226	403,226	403,226
Drying yield	% on bleached pulp	99.2%	99.2%	99.2%
Dried bleached pulp production (dry)	t/year	400,000	400,000	400,000
- consistency 90%	t/year	444,444	444,444	444,444
Lactic acid (LA) production				
H2SO4 consumption (100%)	t/year	-	26,944	26,097
Ca(OH)2 consumption (100%)	t/year	-	20,355	19,715
Gypsum (100%)	t/year	-	37,400	36,225
Fermentation chemicals consumption	t/year	-	19,815	19,192
Lactic acid yield	% on sugar	-	75.0%	75.0%
	% on wood	-	7.7%	7.7%
Lactic acid production	t/year	-	93,480	90,541
Purification yield	% on lactic acid	-	92.0%	92.0%
Lactic acid production, purity 99% (100%)	t/year	-	86,002	83,298
- consistency 85%	t/year	-	101,178	97,998
Power plant				
Energy from recovery boiler	Mcal/hr	315,168	308,101	291,420
Energy from natural gas boiler	Mcal/hr	0	78,125	89,833
Total steam produced (1250 psig)	t/year	4,120,256	5,049,240	4,984,223
Internal steam consumption	t/year	4,120,252	5,049,290	4,984,272
Net steam	t/year	4	-50	-49
Gross power production	MW	75.0	87.7	86.8
Internal power consumption	MW	76.4	90.1	89.0
Net power	MW	-1.4	-2.4	-2.3
	MWh	-11,866	-19,879	-19,036

Table 24 Prices for pulp and lactic acid.

Product prices	Price	Reference
Pulp		
Market price	650 €/t	*Paperage 2013*
Logistic costs	110 €/t	*Malkov 2012*
Price at mill gate	**540 €/t**	
Lactic acid		
Market price	1100 €/t	*Wee 2006*
Logistic costs	110 €/t	*Malkov 2012*
Price at mill gate	**990 €/t**	

Table 25 Unit prices at mill gate.

Unit prices at mill gate	Price	Reference
Wood chips (wet)	50 €/t	*Malkov 2012*
Cooking chemicals:		
NaOH (100%)	480 €/t	*Malkov 2012*
CaCO3 (100%, 30 kg CaCO3/ odt pulp)	20 €/t	*Malkov 2012*
AQ (100%)	3,400 €/t	*Alibaba 2013*
Bleaching chemicals		
MgSO4 consumption (100%)	80 €/t	*Alibaba 2013*
H2SO4 consumption (100%)	230 €/t	*Alibaba 2013*
NaOH consumption (100%)	380 €/t	*Alibaba 2013*
H2O2 consumption (50%)	300 €/t	*Alibaba 2013*
NaCl consumption (100%)	60 €/t	*Alibaba 2013*
NaClO3 consumption (100%)	460 €/t	*Alibaba 2013*
LA production chemicals		
H2SO4 (100%)	35 €/t	*Malkov 2012*
Ca(OH)2 (100%)	120 €/t	*Alibaba 2013*
Fermentation (nutrition, KOH etc.)	100 €/t	*Assumption*
Products		
Pulp	540 €/t	*Calculated*
Lactic acid	990 €/t	*Calculated*
Natural gas for LA production	150 €/1000 m3	*Malkov 2012*
Electricity	40 €/MWh	*Diesen 2013*
Labor (incl. taxes)	15,000 €/year/person	*Diesen 2013*
Maintenance material	6,000,000 €/year	*Reeve 2000*

Market pulp on the market is generally sold as air dried pulp, which has a moisture content of 10%. The lactic acid market price of 1100 €/t (Wee 2006) is somewhat higher than other market prices found for lactic acid 750-970 €/t (Alibaba 2013). When also considering the logistic costs of the product from the mill to the market, the product price is somewhat lower at the mill gate compared

to the market price. Unit prices at the mill gate for wood, chemicals, products, energy, labor and maintenance are presented in **Table 25**. The market price for natural gas of 150 €/ 1000 m³ (Malkov 2012) used in the calculations, is lower than the natural gas price of about 270 €/ 1000 m³ found elsewhere (Indexmundi 2013). The electricity price in Russia fluctuates with time and area. In 2012, the electricity price varied between 1.7 and 9.58 US cents/kWh (Energy Use Calculator 2014), which means about 13-72 €/MWh. The electricity price of 40 €/MWh (Diesen 2012) used in the calculations is about in the middle of this range. The labor costs in manufacturing industries in Russia were 3.61 €/h in 2009 (Grünig, Morschett 2012), which means about 10,400 €/year. Five years later these costs are probably somewhat higher, and therefore the labor costs of 15,000 €/year (Diesen 2013) used in the economic evaluation are realistic.

Table 26 Cash flow for the three processes studied.

Cash flow	Case I Kraft		Case II PE-PS(0.5)AQ		Case III PE-PS(2.0)AQ	
	t/year	€/year	t/year	€/year	t/year	€/year
VARIABLE COSTS		**150,232,684**		**175,034,139**		**171,219,652**
Wood chips (wet)	2,217,600	110,880,000	2,444,400	122,220,000	2,368,800	118,440,000
Cooking chemicals		10,320,000		12,299,040		10,763,520
NaOH (100%)	21,000	10,080,000	17,388	8,346,240	14,784	7,096,320
CaCO3 (100%), 30 kg CaCO3/t pulp	12,000	240,000	12,000	240,000	12,000	240,000
AQ (100%)	0	0	1,092	3,712,800	1,008	3,427,200
Bleaching chemicals		28,558,033		25,450,855		25,451,205
MgSO4 consumption (100%)	275	21,990	204	16,289	204	16,290
H2SO4 consumption (100%)	31,846	7,324,654	26,013	5,983,016	26,014	5,983,112
NaOH consumption (100%)	8,245	3,133,044	8,245	3,132,959	8,245	3,132,985
H2O2 consumption (50%)	14,025	4,207,379	14,024	4,207,260	14,024	4,207,296
NaCl consumption (100%)	15,400	924,023	13,447	806,804	13,447	806,817
NaClO3 consumption (100%)	28,146	12,946,943	24,575	11,304,527	24,575	11,304,707
LA production chemicals		0		3,331,599		3,226,871
H2SO4 (100%)	0	0	26,944	943,048	26,097	913,403
Ca(OH)2 (100%)	0	0	20,355	407,095	19,715	394,298
Ferm. chemicals (nutrition, KOH etc.)	0	0	19,815	1,981,455	19,192	1,919,169
Energy		474,650		11,732,646		13,338,056
Natural gas for LA prod. (m3/year)	0	0	72,917	10,937,500	83,844	12,576,620
Electricity, MWh	11,866	474,650	19,879	795,146	19,036	761,436
FIXED COSTS		**12,750,000**		**13,500,000**		**13,500,000**
Labor		6,750,000		7,500,000		7,500,000
Pulp mill (400 persons)		6,000,000		6,000,000		6,000,000
LA production (50 persons)		0		750,000		750,000
Other (50 persons)		750,000		750,000		750,000
Maintenance material		6,000,000		6,000,000		6,000,000
REVENUES		**240,000,000**		**340,166,520**		**337,017,831**
Bleached pulp (90%)	444,444	240,000,000	444,444	240,000,000	444,444	240,000,000
Lactic acid (85%)	0	0	101,178	100,166,520	97,998	97,017,831
Cash flow, €/year		**77,017,316**		**151,632,381**		**152,298,179**

4.10.3 Costs, revenues and cash flow

The variable costs, fixed costs and revenues were determined for the processes based on the simulation results and the unit prices (**Table 26**). The calculated cash flow values show that the kraft process has a positive cash flow of about 77 million €/year, but that for both cases of lactic acid production the cash flow increases remarkably to about 150 million €/year. This means that the larch biorefinery process increases revenue by about 73 million €/year.

4.10.4 Sensitivity analysis

The key parameters influencing the cash flow of these processes are wood price, pulp price and price of lactic acid. Sensitivity analyses of +/- 25% were determined for the processes. Minimum (-25%) and maximum (+25%) prices for

Table 27 Prices used in the sensitivity analysis.

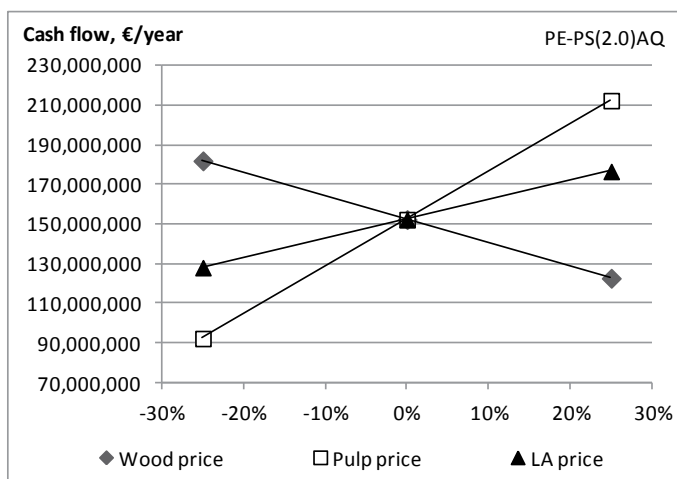| Prices	At mill gate	-25%	+25%
Wood	50.00	37.50	62.50
Pulp	540.00	405.00	675.00
Lactic acid	990.00	742.50	1237.50

Figure 15 Sensitivity analysis of +/- 25% of wood, pulp and lactic acid prices for the PE-PS(2.0)AQ process (Case III).

wood, pulp, and lactic acid were calculated, and are presented in **Table 27**. The cash flows were then determined for the different prices. For example, when determining the cash flow for pulp price of -25%, the pulp price of 405 € was used, while the other prices were kept unchanged. **Figure 15** presents the sensitivity analysis of the PE-PS(2.0)AQ process (Case III), and shows that the pulp price influences the cash flow most, but the wood price is also an important parameter when looking at the economy of this process. The sensitivity analysis for the PE-PS(0.5)AQ process (Case II) would be similar.

4.10.5 Investment costs

The investment costs for the pre-extraction and hydrolysis units, MOXY reactor and natural gas boiler were available at similar scales in the literature, and could therefore be directly used in the evaluation. The costs for the fermentation and purification units were re-scaled to the present size according to **Equation 2**, where n is an equipment specific index (0.8 for electrodialysis) (Garde 2002).

$$New\ cost = Original\ cost * (New\ size/\ Original\ size)^n \qquad \textbf{Equation 2}$$

The total scaled investment costs for the biorefinery processes are estimated to be 105,000,000 € (**Table 28**). Smaller investment costs should also be reserved for the handling of the by-product gypsum. The cash flow determines the size of the investment which can implemented. As a rule, the investment costs should certainly be less than five times the annual cash flow. Comparing the investment costs to the cash flow values in Case II and III shows that the payback time for the investment costs would be about 16 months.

Table 28 Estimated investment costs for additional units in a larch biorefinery

Investment costs	Price	Reference
Pre-extraction and hydrolysis	25,000,000 €	Mao 2010
Fermentation and purification	50,000,000 €	Datta1995
MOXY unit	15,000,000 €	Malkov 2012
Natural gas boiler	15,000,000 €	Blomberg 2013
Total	105,000,000 €	

4.11 Summary of results

The relevant results of this research project summarized below.

4.11.1 Pre-extraction

Water pre-extraction (PE) of Siberian larch chips removes sugars from the wood at lower temperatures than other softwoods (**Paper I, Paper II, Paper III**). Different PE temperatures were tested (**Paper II**). Based on the composition of the extracts and the extracted chips, a detailed mass balance was presented for the water PE. From the mass balance the dissolution behavior of the different hemicelluloses and lignin with varying temperature and time were quantified. The ideal conditions for water PE would be to dissolve arabinogalactan without significant removal of xylan and glucomannan in order to retain the yield in the final kraft pulp. According to the results the optimal PE conditions would be at 140-150 °C for 60-90 min and leading to dissolution of about 10% of the sugars (**Paper II**). PE at 150 °C for 90 min dissolves 11.2% on wood of sugars (**Paper III**).

4.11.2 Washing of extracted chips

A mild wash between pre-extraction (PE) treatment and PSAQ pulping is sufficient to achieve efficient delignification during pulping, and to increase the amount of recovered sugars (**Paper III**). The amounts of carbohydrates removed during PE and mild washing are 11% and 5%, respectively. The combined stream would contain 10.2% (on original wood) of sugars for production of value added products such as lactic acid.

4.11.3 PE-PSAQ pulping

The removal of hemicelluloses prior to pulping results in yield loss. Polysulfide (PS) and anthraquinone (AQ) can be used as pulping additives in order to maintain the pulp yield (**Paper I, Paper III**). PS and AQ increase pulp yield by oxidizing the reducing end groups of polysaccharides to aldonic acid groups, thus stabilizing the polysaccharides against peeling reactions. Besides the yield increase, AQ accelerates the delignification rate of pulping by fragmenting and dissolving lignin. In softwood PS pulps the higher retention of glucomannans and in AQ pulps the preservation of mainly cellulose enhance the yield respectively. A synergism exists when PS and AQ are used together in alkaline pulping. By using

a PS charge of 2% and an AQ charge of 0.1% the pulp yield loss is reduced to 2%, compared to 5% for a PE kraft cook with no additives used (**Paper III**). After pre-extraction (PE) lower alkali charges and H-factors can be used in the subsequent pulping process (**Paper I**).

The viscosities of the unbleached pre-extracted kraft pulps were higher than those of unbleached conventional larch kraft pulps. Somewhat lower strength and optical properties for unbleached pre-extracted PSAQ pulp were obtained compared to unbleached conventional larch kraft pulp. (**Paper I**)

The total dry solids content of the pre-extracted PSAQ black liquor is somewhat lower than that of conventional kraft black liquor (normally about 20%), representing a reduction in recovery boiler load (**Paper I, Paper III**). Because of the very similar organics to inorganics ratio, it is unlikely that the burning properties of black liquor will be affected when converting from conventional kraft to the PE-PSAQ process for larch wood (**Paper III**).

4.11.4 Paper properties

Comparisons between O-D0-Ep-D2-P bleached PE-PSAQ paper and kraft paper of larch wood showed that the PE-PSAQ process does not affect the paper properties negatively (**Paper IV**). Instead, most properties were similar or even better than the properties of the larch kraft paper. The properties of the PE-PSAQ paper were also compared to paper properties of other softwood species. Based on this comparison the larch PE-PSAQ pulp could be used for similar paper products such as spruce or pine kraft pulps for packaging boards and papers and also as reinforcement pulp.

4.11.5 Fermentation

Fermentation of acid hydrolyzed hemicelluloses-rich larch extracts with *Bacillus coagulans* MXL-9 gave attractive results (**Paper II**). Fermentation of extracts containing less sugar results in poorer yield. Enzymatic treatment in combination with fermentation is not a good alternative for larch extracts. In all cases, all five monosugars were consumed by the bacteria and converted into mainly lactic acid. The lactic acid yield for the extract produced at 160 °C for 120 min approached 80%. This shows that there is potential for converting the hemicellulose-rich larch extract into lactic acid.

Also eight other bacteria strains were tested to produce different products from the larch extract through fermentation (**Paper IV**). In general *Lactobacillus* strains metabolized sugars of larch extract faster than *Clostridium* strains. The tested strains have different sugar specificity: *L. plantarum* DSM 20314 fermented all hydrolyzed larch extract (HLE) sugars except xylose; *L. brevis* strains did not utilized mannose; *B. coagulans* and the *Clostridium* strains (except for *C. acetobutylicum* MSU 7) metabolized all HLE sugars; *C. acetobutylicum* MSU 7 fermented larch extract very weak. Lactate production by *L. plantarum* DSM 20314 gave the most attractive result from the experiments with these eight bacteria strains.

4.11.6 Technical and economic evaluation

A process flow chart for a larch biorefinery process was designed and presented (**Paper V**). The process is based on water pre-extraction of the larch wood chips before pulping with polysulfide (PS) and anthraquinone (AQ). About 10.2% sugar on wood is recovered through pre-extraction. The recovered sugars are fermented into lactic acid.

An existing kraft pulp mill could relatively easy be converted into a larch biorefinery. For the pre-extraction and the lactic acid production the following additional process units are needed: extraction, hydrolysis and neutralization, fermentation, purification and a natural gas boiler. For the preparation of the PS liquor a MOXY unit is needed. Two slightly different larch biorefinery processes were compared with a conventional kraft process.

Mass and energy balances were obtained through simulation. The cash flows were determined for each process case, and it showed that an additional lactic acid production for a kraft pulp mill would be profitable. The sensitivity analysis shows that the pulp price has the biggest effect on the economy of the PE-PS(2.0)AQ process. The investment costs could be paid back within 16 months, when adding a lactic acid production part to an existing pulp mill (**Paper V**).

A combined pulp and lactic acid production using larch wood as raw material would have potential, both technically and economically.

5 CONCLUSIONS

This thesis presents a concept for a larch biorefinery. Hemicelluloses are removed from the larch wood chips by water pre-extraction prior to pulping. The sugars in the extract are fermented into lactic acid. Pulp remains the main product, while lactic acid becomes an additional product.

Proof of concept for a larch biorefinery was confirmed based on preliminary experiments. A significant amount of sugars can be removed by water pre-extraction. It is possible to compensate the yield loss caused by the pre-extraction by using anthraquinone (AQ) and polysulfide (PS) as pulping additives. The dissolved sugars can efficiently be fermented into lactic acid.

Relevant process stages were thoroughly investigated and the optimal conditions were determined. The characteristics of larch hemicelluloses allow rather low pre-extraction temperatures in order to remove a significant amount of sugars. At the ideal pre-extraction temperature of 150 °C arabinogalactan dissolves, while xylan and glucomannan remain in the wood in order to retain the pulp yield on original wood in the final kraft pulp. Pre-extraction at 150 °C for 90 min dissolves 11% sugars on wood. A mild wash of the pre-extracted wood chips is needed to remove the dissolved sugars from the wood chips in addition that which is obtained by drainage. At a PS charge of 2% and 0.1% AQ on wood the overall pulp yield loss is reduced to just 2% relative to conventional kraft pulp. Without PS and AQ addition the pulp yield loss is 5%.

A process scheme for a larch biorefinery was designed. The developed process is based on practical conditions and equipment available on the market. Steady-state material and energy balance process models were produced using WinGEMS V.5.3. The process was both technically and economically evaluated. According to the cash flow the suggested larch biorefinery concept would pay back the needed investments within about 16 months. This confirms that this kind of larch biorefinery would have potential.

Below are the answers to the research questions of this study:

1. Is there potential for pre-extraction pulping of larch wood?

   Yes, there is. A significant part of the hemicelluloses in larch wood can rather easily be removed by water pre-extraction (PE). By using anthraquinone (AQ) and polysulfide (PS) as pulping additives the yield loss caused by the pre-extraction can be mostly compensated. The PE PSAQ pulps are easier to bleach than kraft pulp, and the pulp quality is not harmed. The sugars removed by PE can efficiently be fermented into lactic acid.

2. Which are the ideal extraction and pulping conditions?

   Based on the experiment of this research the pre-extraction temperature of 150 °C for 90 min is ideal for larch wood. At these pre-extraction conditions 11% sugars on wood dissolves. Mostly the arabinogalactan dissolves which otherwise would be fully removed anyway during regular kraft pulping, while xylan is mostly retained. A mild wash of the pre-extracted chips is sufficient to remove most of the dissolved sugars from the wood. PS and AQ should be used as pulping additives in order to maintain the pulp yield. Generally, the pulping conditions can be somewhat milder compared to a conventional kraft cook.

3. What is the mechanism of hemicellulose dissolution during extraction?

   More wood material is dissolved with increasing extraction temperature and time. The extracts mainly consist of galactan. At temperatures up to and including 120°C only galactan and arabinan are dissolving as oligomers, but at temperatures above 140°C xylan and mannan oligomers also appear in the extracts. The finding that only arabinogalactan dissolves at 120°C or lower can be explained by its high solubility. At 160°C, the extracts contain a significant amount of mostly oligomeric glucomannan and xylan. Thus to preserve these hemicelluloses in the extracted wood, the ideal extraction temperature would be about 150°C.

4. How could the process be optimized and performed in practice?

The optimal conditions for the relevant process units, i.e. pre-extraction, washing of pre-extracted chips, PSAQ pulping and fermentation to lactic acid, were optimized. A combined pulp and lactic acid producing mill could be built as a greenfield mill, or preferably a pre-extraction unit and a lactic acid production site could be added to an existing pulp mill. The larch biorefinery process developed in this research is based on practical conditions and process equipment available on the market.

5. What are the qualities of the products?

The PE PSAQ process does not affect the pulp quality negatively, and the results show that bleached PE PSAQ larch pulp can be used for similar applications as pine and spruce pulps, i.e. mainly paper for packaging or newspaper. The extracted hemicelluloses can efficiently be fermented into lactic acid.

6. What are the economic aspects for this process concept?

The economic evaluation of the PE PSAQ process gave very attractive results. The cash flow increases by a factor two when a lactic acid production line is added to an existing pulp mill. The payback time for the required investments to produce lactic acid is rather short, only about 16 months.

There are certain limitations and challenges with this kind of a larch biorefinery. As raw material this larch biorefinery uses larch wood, which is mainly available in the Siberia region in Russia. When the raw material in question is wood, the production site should naturally be located close to the raw material resources. Therefore, the Siberia region should be a suitable location for this larch biorefinery, preferably not too far from China which would a large market for the produced products, pulp and lactic acid. The presented larch biorefinery process is a good example for how a traditional mill rather easily can increase its revenue with an additional new product.

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