Helsinki University of Technology Laboratory of Pulping Technology
Reports, Series A29
Espoo 2002

STUDIES ON LIQUID PENETRATION INTO SOFTWOOD CHIPS - EXPERIMENTS, MODELS AND APPLICATIONS

Sergey Malkov

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Forest Products Technology, Helsinki University of Technology for public examination and debate in Council Room at Helsinki University of Technology (Espoo, Finland) on the 22nd of November, at 12 noon.

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UNIVERSITE DE TECHNOLOGIE D'HELSINKI	http://www.hut.fi/Units/Pulp/

Distribution:

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P.O. Box 6300
FIN-02015 HUT, Finland
Tel. + 358 9 4511
Fax + 358 9 451 4259

ISBN 951-22-6193-6
ISSN 1457-750X

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Otamedia Oy
Espoo

HELSINKI UNIVERSITY OF TECHNOLOGY
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http://www.hut.fi

ABSTRACT OF DOCTORAL DISSERTATION

Author Sergey Malkov

Name of the dissertation

Studies on Liquid Penetration into Softwood Chips - Experiments, Models and Applications

Date of manuscript 30.05.2002	Date of the dissertation 01.11.2002
☐ Monograph	☑ Article dissertation (summary + original articles)

Department	Department of Forest Products Technology
Laboratory	Laboratory of Pulping Technology
Field of research	Pulping Technology
Opponent(s)	Professor Adriaan van Heiningen and Professor Kaj Henricson
Supervisor	Professor Panu Tikka
(Instructor)	Emeritus Professor Johan Gullichsen

Abstract

Latest developments in chemical pulping have been mainly driven by advances in pulping chemistry, disregarding the phenomena that take place at the front-end of cooking. In spite of the existence of several concepts and theories, some aspects still remain unclear and more research is needed to achieve a complete understanding of the process of liquid penetration into wood chips. The objectives of the present thesis were to provide more knowledge on the process of liquid penetration into softwood chips and the factors affecting it, to develop a model of penetration process and to evaluate the efficiency of chip presteaming.

It was found that the nature of the liquid and its properties play an important role in determining the efficiency of penetration. By optimizing the process conditions and applying certain “penetration aid” techniques, such as presteaming, it is possible to significantly improve the efficiency of penetration and to achieve a higher final penetration degree. Based on experimental data, a mathematical model was developed for the process of water penetration into softwood chips under isothermal conditions. The model was found to predict accurately the course and final level of penetration of water and fresh cooking liquor (white liquor) into the chips under defined conditions. However, the suggested model cannot be used as a general model for predicting the penetration of spent cooking liquor (black liquor).

Chip presteaming was examined from the viewpoint of the chip heating and air escape processes. A three-dimensional model was proposed to estimate the efficiency of heating the single chip by saturated steam. It was shown that the time required to heat the single chip with steam was very short, only a few minutes. However, the process of air removal proceeds considerable slower than chip heating process. Achieving a high degree of air removal may require quite long steaming times, up to an hour, especially with heartwood chips. Complete removal of air, however, may be difficult to achieve, even by applying optimal steaming conditions and long steaming times.

The knowledge acquired about the efficiency of penetration and presteaming processes was applied to examine contemporary cooking technology. Presteaming of the chips and application of a higher-pressure profile at the front-end of kraft displacement batch cooking resulted in reductions in the amount of rejects and the kappa number of the bulk pulp as well as improved uniformity of delignification.

Keywords Penetration, softwood chips, presteaming, modelling, kraft pulping

UDC	Number of pages 64
ISBN (printed) 951-22-6193-6	ISBN (pdf) 951-22-6194-4
ISBN (others)	ISSN 1457-750X

Publisher Helsinki University of Technology, Laboratory of Pulping Technology

Print distribution Helsinki University of Technology, Laboratory of Pulping Technology

☑ The dissertation can be read at http://lib.hut.fi/Diss/

To My Family

ACKNOWLEDGEMENTS

I am very grateful to my supervisor Professor Panu Tikka for his encouragement and guidance as well as for many valuable discussions during the course of this work. Special thanks are due to Emeritus Professor Johan Gullichsen, my earlier supervisor and instructor, for encouraging and backing me up with his constant confidence in this work.

Many other people have contributed to this study. In particular, I wish to express my deepest gratitude to Dr Valerii Kuzmine and Dr Vladimir Baltakhinov for their co-operation and valuable suggestions. Stimulating discussions were essential in this research work. In this respect, I would like to thank Kari Kovasin (Sci-Tech Service Ltd.), Prof. Richard Gustafson (University of Washington) and Prof. Tapani Vuorinen (Helsinki University of Technology). I am thankful to Sirpa Lindholm and Carl-Anders Lindholm for their kind help and for sharing their wisdom of life. I am also indebted to all members of the Laboratory of Pulping Technology for creating a positive and inspiring working atmosphere, and for many happy moments that we shared at work and outside of it. It was a great pleasure to work with you.

I thank my lovely parents and brother for their encouragement and understanding during these years. I also wish to thank my friends in Finland and all over the world for their support. My dearest thanks are due to Sari for her love and understanding.

Financial support from the Technology Development Centre of Finland (TEKES), UPM-Kymmene Oyj, Stora Enso Oyj, OY Metsä-Botnia AB, and Metso Corp. is gratefully acknowledged. This work has been carried out under the International Ph.D. Programme in Pulp and Paper Science and Technology (PaPSaT).

Otaniemi, October 2002

Sergey Malkov

LIST OF PUBLICATIONS

This dissertation is mainly based on the articles listed below and included in the appendix. The papers are referred to in the text with the Roman numerals I-VII.

I. Malkov, S., Tikka, P. and Gullichsen, J.: Towards complete impregnation of wood chips with aqueous solutions. Part 1: A retrospective and critical evaluation of the penetration process. Paperi ja Puu: in press.

II. Malkov, S., Tikka, P. and Gullichsen, J.: Towards complete impregnation of wood chips with aqueous solutions. Part 2: Studies on water penetration into wood chips. Paperi ja Puu 83(2001):6, 468 - 473.

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

IV. Malkov, S., Tikka, P. and Gullichsen, J.: Towards complete impregnation of wood chips with aqueous solutions. Part 4: Effects of front-end modifications in displacement batch kraft pulping. Paperi ja Puu: in press.

V. Malkov, S., Tikka, P., Gustafson, R., Nuopponen, M. and Vuorinen, T.: Towards complete impregnation of wood chips with aqueous solutions. Part 5: Improving uniformity of kraft displacement batch pulping. Paperi ja Puu: in press.

VI. Malkov, S., Kuzmin, V.A., Baltakhinov, V.P. and Tikka, P.: Efficiency of chip presteaming – result of heating and air escape processes. Nordic Pulp and Paper Research Journal: in press (Issue 4 of 2002).

VII. Malkov, S., Kuzmin, V.A., Baltakhinov, V.P. and Tikka, P.: Modelling the process of liquid penetration into softwood chips. Journal of Pulp and Paper Science: in press (April 2003 issue).

In addition, some unpublished results are presented in Appendices A - C.

AUTHOR'S CONTRIBUTION

This thesis is based on the results of a research project carried out at the Laboratory of Pulping Technology of Helsinki University of Technology during the years 1998 - 2001 under the supervision of Dr Panu Tikka and Dr Johan Gullichsen. The main contributions of the thesis are:

- Determination of the efficiency of penetration of water and cooking liquors into softwood chips under different conditions with the use of a new laboratory device;
- Development of the model of water penetration into softwood chips;
- Determination of efficiencies of wood chip heating and air escape during presteaming of chips;
- Evaluation of the effect of modified front-end conditions of kraft displacement batch cooking.

The author has had an active role at all stages of the work reported in the publications and Appendices A-C. The author has planned and written all the publications (I-VII). Paper I evaluates the penetration process from the retrospective standpoint of industrial development and research and gives a summary of currently available knowledge concerning the penetration of aqueous solutions into wood chips.

Papers II & III describe the results of experiments concerning water and black liquor penetration into softwood chips. The author carried out the experimental work.

Paper IV examines the effect of modifying the front-end conditions of kraft displacement batch cooking on cooking performance, bleachability and papermaking potential of the pulp. The author planned and carried out the experimental work. Basic laboratory analyses were performed with the help of laboratory assistants indicated in the acknowledgements.

Paper V deals with the issue of improving the uniformity of pulping. The author carried out the cooking trials. The fibre kappa distributions were measured at the University of Washington under the supervision of Dr Richard Gustafson (co-author). The FTIR spectral measurements were carried out under supervision of Mrs Mari Nuopponen and Dr Tapani Vuorinen (co-authors). The author of this thesis planned the measurement campaigns, made the data analyses and performed the interpretation of the results.

Papers VI & VII discuss the chip presteaming and liquid penetration processes from the mathematical viewpoint. Discussions are based on the author's experimental work and the knowledge available in the literature. The author carried out the modelling work in co-operation with Dr Valerii Kuzmine (co-author). Dr Vladimir Baltakhinov (co-author) was responsible for mathematical solutions.

LIST OF SYMBOLS AND ABBREVIATIONS

Mathematical symbols

- A - factor determining the area of phase border
- C - air concentration in liquid
- C_P - specific heat capacity of wood chip
- D - diffusion coefficient of dissolved air in water
- D_a - diffusion coefficient of air (gaseous phase)
- H - Henry´s constant
- K - specific permeability of wood chip
- K_g - permeability of wood chip to gases
- K_x - longitudinal permeability coefficient
- K_z - radial permeability coefficient
- L - length of the specimen in the flow direction
- L_x - half-length of the chip
- L_y - half-width of the chip
- L_z - half-thickness of the chip
- M - molecular weight of liquid
- N - amount of entrapped air in gaseous mixture
- ΔP - pressure differential
- P_a - partial pressure of air
- P_c - capillary pressure
- P_{ex} - external pressure
- P_g - pressure of gaseous mixture
- P_h - hydrostatic pressure
- P_v - partial pressure of water vapour
- T - temperature of penetration process
- U - velocity of liquid movement
- U_x - velocity of longitudinal movement of liquid
- U_z - velocity of radial movement of liquid
- X - fraction of void volume penetrated by liquid through longitudinal direction
- Z - fraction of void volume penetrated by liquid through radial direction
- c - air concentration in gaseous phase
- k - proportionality constant
- l - distance from the liquid-gas interface
- n_a - amount of air escaped from the gas phase through the unit area
- r - effective radius of capillary
- t - time
- u - rate of air flow
- x - spatial coordinate (longitudinal direction)
- y - spatial coordinate (tangential direction)
- z - spatial coordinate (radial direction)

- α - viscous resistance coefficient
- β - inertial resistance coefficient
- γ - surface tension of water
- η - permeability ratio
- φ - wetting angle
- λ_x - thermal conductivity of chip (longitudinal)
- λ_y - thermal conductivity of chip (tangential)
- λ_z - thermal conductivity of chip (radial)
- μ - dynamic viscosity of liquid
- μ_a - dynamic viscosity of air
- θ - dimensionless temperature
- ρ_{ch} - basic density of wood chips
- ρ_l - density of liquid

Abbreviations

BL	Black liquor
DS	Dry-solids
$D_0ED_1ED_2$	Bleaching sequence (D - chlorine dioxide stage, E - alkaline extraction stage)
EA	Effective alkali
FTIR	Fourier-transform infrared
PD	Penetration degree
RA	Reinforcement ability
WL	White liquor

DEFINITIONS

"Black box" model	is a model that describes a process that is unknown and on which only empirical knowledge and data are available.
Black liquor	is the residual liquor from the kraft cooking process containing spent chemicals and wood residues.
Bleachability	is a qualitative term describing the relative ease with which pulp can be bleached. The bleachability can be expressed in terms of brightness development versus equivalent chlorine multiple or kappa factor.
Compression level	is defined here as the maximum penetration degree that can be achieved under defined process conditions assuming that no air escapes from the chip voids during the penetration.
Delignification	is the removal of all or part of the lignin from wood or plant material by chemical treatment.
Displacement batch cooking	is a term used for industrial modified kraft pulping in a batch mode with black liquor displacement. Examples of displacement batch cooking systems are the RDH and SuperBatch processes.
Effective alkali	is the amount or concentration of sodium hydroxide (NaOH) plus one-half of the sodium sulphide (Na_2S), both expressed in the same units. In this work the effective alkali is expressed as sodium hydroxide.
"Grey box" model	is a model that describes a process based on fundamental laws combined with empirical correlations.
Impregnation	is the process of distributing cooking chemicals through the wood chips by mechanisms of penetration and diffusion.
Penetration	refers to the flow of liquid into air-filled voids of the wood chip under the pressure gradient.
Penetration degree	is defined here as the fraction of the void volume within the wood chips occupied by liquid.
Reinforcement ability	is a parameter that characterises the papermaking potential of pulp. It is defined as the fibre length divided by fibre coarseness and multiplied by the tear index of the pulp.
White liquor	is a kraft cooking liquor containing the active alkali components of sodium hydroxide (NaOH) and sodium sulphide (Na_2S).

TABLE OF CONTENTS

1. INTRODUCTION

1.1 Retrospective view on the development of pulping systems

A retrospective view on the development of pulping systems and the front-end of the cooking process is presented schematically in Figure 1. The main features of sulphite and kraft pulping processes were already established at the end of the 19th century. Wood chips were cooked in rotating reactors. A big break-through was the transition to stationary batch digesters during the 1910s. Then, until the 1950s, the development of cooking systems involved mainly increasing the size of digesters and optimising the stages and conditions of the process.

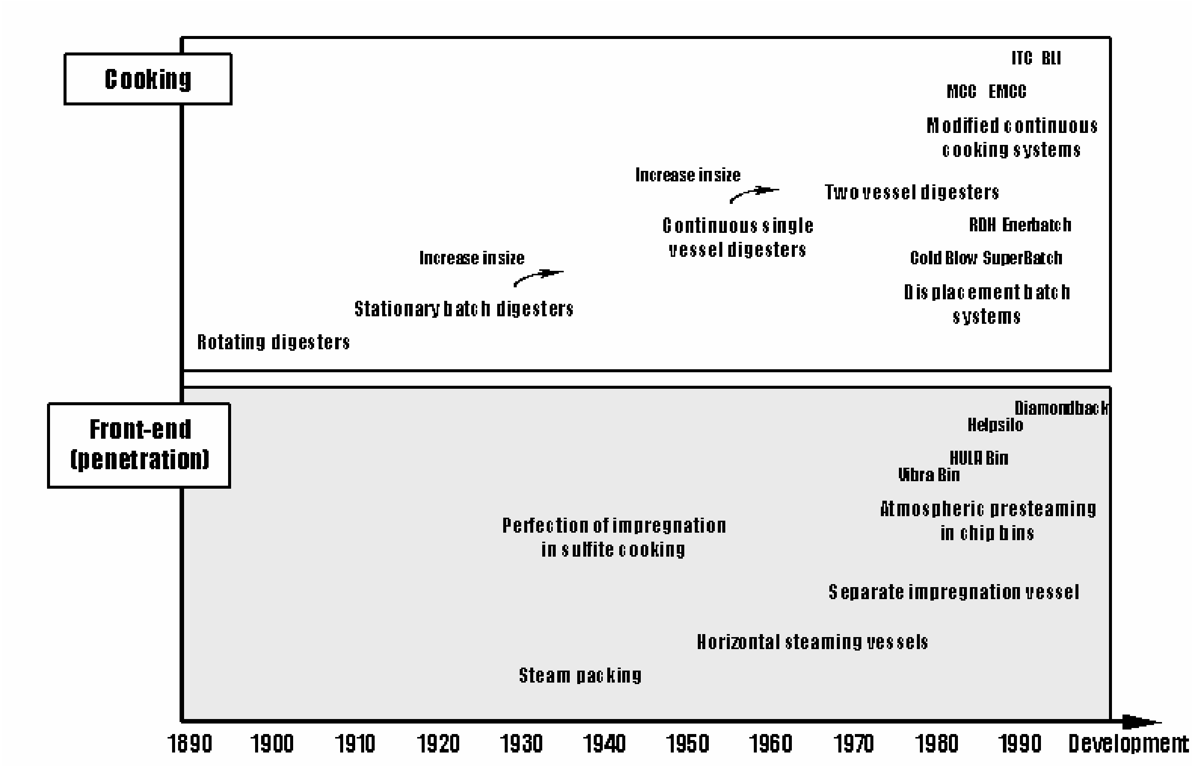

Figure 1. Retrospective view on the development of pulping systems [I].

The need for efficient transport of chemicals into the wood chip matrix prior to cooking was already emphasized in the early 1920s [1]. During the 1930s and 1940s, however, the interest of scientists was mainly focused on sulphite pulping [2-4] because of the serious concerns related to the "burnt cook" phenomenon [3,5]. As a result of several studies, the impregnation stage of the industrial sulphite cooking process was gradually perfected. However, the advances in the front-end technology, such as chip presteaming, were seldom applied to the kraft process due to a number of reasons [I].

During the 1950s, following the development of continuous systems that had a shorter impregnation time, the question of efficient impregnation in kraft cooking was brought up, especially in relation to softwood chips. This triggered research aiming at optimising the conditions for penetration and diffusion of kraft liquor into the wood chips, as well as application of pre-treatments to enhance these processes. Several advances in continuous kraft technology took place during the late 1960s - early 1970s, which had some success in addressing the problem of inefficient penetration [I]. These included development of two-vessel systems with a separate impregnation vessel and atmospheric chip bins. Continuous cooking remained the mainstream of digester design until the 1980s, when the concept of "modified kraft cooking" was developed in Sweden [6]. Since then, some of the principles of "modified cooking" have been utilized for developing the batch kraft pulping technology, resulting in several new competitive processes. The "modified cooking" concept was also applied to continuous technology [I].

The last couple of decades have been characterised by a burst of research activity in the area of pulping chemistry and the latest stages of the process (back-end of cooking). In contrast, the basic phenomena that take place at the front-end of cooking have barely attracted attention among scientists. As a result, the latest developments in kraft cooking have mainly been driven by advances in pulping chemistry, disregarding the front-end issues. In spite of the fact that recent trends in cooking processes would require more effective penetration and diffusion of reactive chemicals into the wood chips [I], the front-end technology has remained practically unchanged for the past few decades (Figure 1).

A number of studies have been carried out in the past to examine the process of liquid penetration into wood. Different techniques have been used to obtain experimental data about this process [I]. Practically all these techniques have had their own drawbacks and limitations. By using them, however, researchers have been able to obtain direct and indirect quantitative information on the amount of penetrated liquid and the penetration rates as well as qualitative information about the ways of liquid penetration into wood. As a result, several concepts and theories related to the transport of liquid in wood were introduced. This knowledge helps to understand some of the phenomena that take place during the flow of liquid into the wood matrix, the factors affecting the penetration of liquid and ways how to improve it. However, a lot of aspects remain unclear and more research is needed to achieve a better understanding of the process of liquid penetration. The need for new reliable and accurate methods that are able to provide direct continuous data on the process of liquid penetration also has to be emphasised.

1.2 Objectives and structure of the thesis

Since a complete solution to the liquid penetration mechanism and all phenomena accompanying it is too large a target for a work of this scope, more realistic objectives were set. These were:

1) to provide more knowledge on the process of liquid penetration into softwood chips and factors affecting it,
2) to develop a simple model of the process of water penetration into softwood chips,
3) to evaluate the chip presteaming technique from the viewpoints of chip heating and air escape,
4) to examine the effects of improved front-end conditions in kraft displacement batch cooking.

The structure of the thesis is shown as a block diagram in Figure 2.

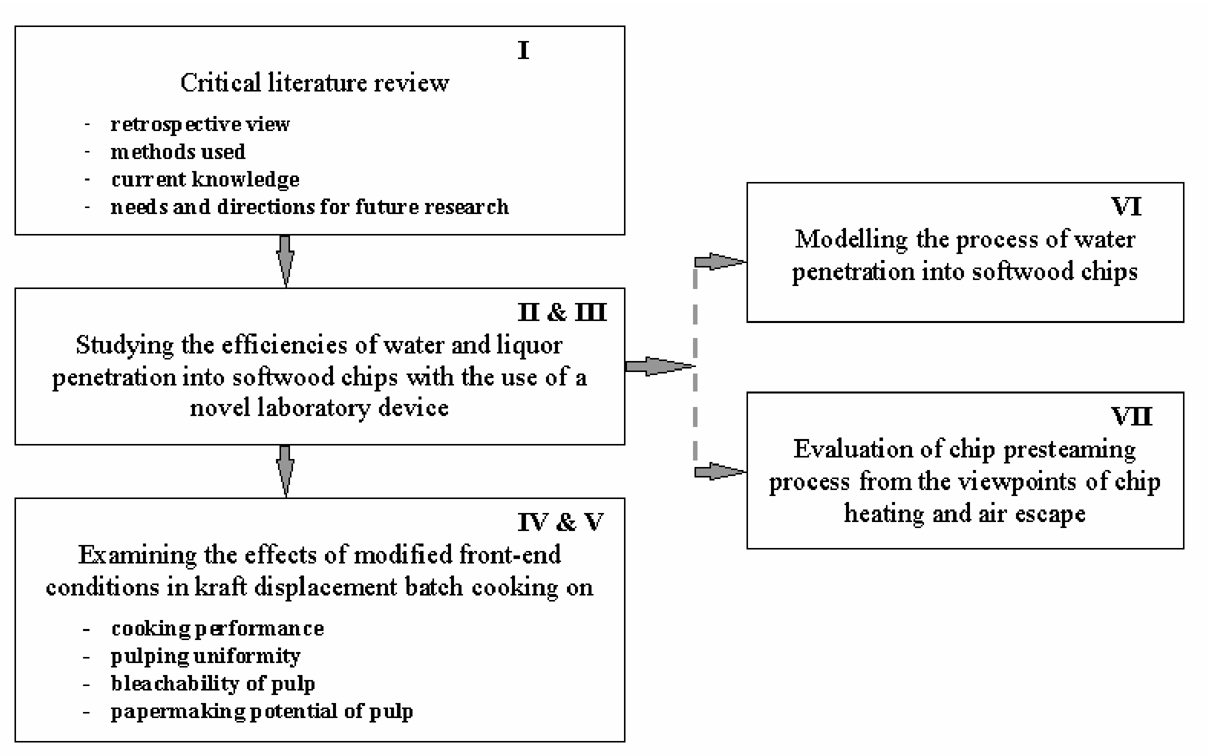

Figure 2. Structure of the thesis. Roman numerals refer to publications.

2. MATERIALS AND METHODS

The handmade softwood chips used in the penetration experiments were prepared from three softwood species: pine (*Pinus silvestris*), spruce (*Picea abies*) and larch (*Larix sibrica*). Most of the results included in this thesis, however, were obtained from the experiments with pine chips. Chips with different dimensions were separately prepared from the sapwood and heartwood portions of a log, as described in Paper II. The length of the chips corresponded to the longitudinal direction of the stem, the width and thickness to the tangential and radial directions, respectively. The chips did not contain bark or knots. The moisture content and basic density of sapwood and heartwood chips were determined before the experiments with SCAN standards [II, III, VI, VII].

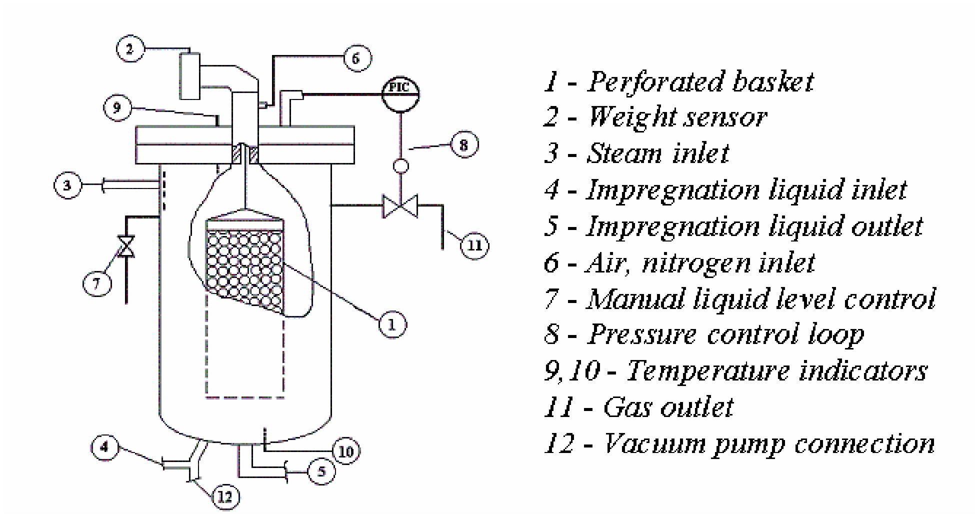

Figure 3. Laboratory impregnator [II].

Penetration experiments were performed with a specially designed laboratory impregnator. A perforated basket containing the chip sample was connected to a weight sensor, which allowed the chip sample weight to be estimated throughout the experiment on a continuous basis (Figure 3) [II]. Based on the sensor readings and the properties of the chips and penetrating liquid, the penetration degree expressed as the fraction of the voids within the chips filled by liquid was calculated at certain time intervals. A more detailed description of the laboratory impregnator and the method can be found in Papers II and III. Most of the penetration experiments were carried out with water under different process conditions. Penetration of white and black liquors into pine chips was also studied [III, Appendix B]. Properties of the liquors, such as density, surface tension and dynamic viscosity, were measured before the experiments with methods mentioned in Appendix B.

Some of the handmade pine chips were laminated by applying a thin layer (0.5 mm) of epoxy-paint and used together with original chips to examine the efficiency of chip heating by saturated steam. The procedure for these experiments is described in Paper VI.

Industrial pine chips were used in kraft displacement batch cooking simulations. The chips were classified in the laboratory in accordance with the standard SCAN-CM 40:94. Only two chip fractions were used in cooks: over-thick chips and accept chips in proportions of 5 % and 95 %, respectively. More detailed information about the properties of the pine roundwood used and the chip preparation method can be found in Papers IV-V. Cooking experiments were carried out at the Helsinki University of Technology. The laboratory digester used for cooks was similar to the one described elsewhere [7]. This cooking system enabled simulating cooking stages, displacement times and circulation rates comparable to those of mill-scale kraft displacement batch processes. Chip samples were cooked in accordance to different scenarios with different front-end conditions, while other cooking conditions were kept constant [IV-V]. The cooking results were evaluated based on the yield and amount of rejects as well as basic pulp properties. The kappa number, viscosity and ISO brightness of the pulps were measured according to SCAN standards.

To study the effect of front-end conditions on the bleachability and papermaking potential of pulp, some pulp samples were bleached using oxygen delignification and the sequence $D_0ED_1ED_2$ with varying chlorine dioxide charges [IV]. Bleached pulp samples were used for preparation of handsheets and testing of paper and pulp properties. Experimental procedures and testing methods are discussed in Paper IV.

In this thesis, the effect of front-end conditions in displacement batch cooking on the uniformity of delignification was examined through two approaches [V]. In the first approach, the kappa numbers of single fibres and their distribution were studied. A pulp sample from every cooking scenario was analysed by using the flow-through fluorescence image analyser at the University of Washington. A detailed description of the apparatus and method is given elsewhere [8]. In the second approach, the kappa number distribution within the cooked handmade pine chips was assessed with Fourier-transform infrared (FTIR) spectroscopy. The equipment and procedure for FTIR measurements as well as the method for test-piece preparation are described in Paper V. Infrared spectra were calibrated to traditional wet-lab analysis of the kappa number. The calibration procedure and FTIR data analyses are also discussed in Paper V.

3. LIQUID PENETRATION INTO SOFTWOOD CHIPS

3.1 Background

The objective of chemical pulping is to dissolve lignin in wood in order to release the fibres from the wood matrix [9]. To ensure proper fibre separation, it is important that chemicals are transported to reaction sites uniformly and rapidly enough. Ideally, each fibre should receive the same amount of chemical treatment for the same time at the same temperature. Thus, the effective mass transfer of reactive chemicals into wood chips is of utmost importance for chemical pulping processes. During impregnation, reactive chemicals are transferred into the core of the wood by two primary mechanisms, which are entirely different and operate in response to different laws [10]. The first mechanism, liquor penetration, refers to the flow of liquor into the air-filled voids of the wood chip, under the pressure gradient. The second mechanism, diffusion, refers to the movement of ions or other soluble matter through water under the influence of the concentration gradient. Wood chips used in chemical pulping processes are practically never oven-dry or water-saturated. This means that a combination of penetration and diffusion will occur when chips of normal moisture content are treated with liquor at elevated temperatures and pressures. This thesis, however, deals only with the issues related to the penetration process.

Forced penetration of liquid into the capillaries of the wood chip takes place due to the pressure gradient [11]. Usually, wood chips represent a three-phase system consisting of solid wood substance, water and some amount of gases, mainly air, present within their voids. In this case, the pressure differential can be considered as the difference between the sum of external, hydrostatic and capillary pressures and the total pressure of the gaseous mixture within the wood voids (*Eq.1*). Here, the external pressure is the sum of the ambient pressure and the over-pressure applied.

$$\Delta P = \left(P_{ex} + P_h + P_c\right) - P_g \qquad \textbf{(1)}$$

where

ΔP	is	pressure differential,
P_{ex}		external pressure,
P_h		hydrostatic pressure,
P_c		capillary pressure,
P_g		pressure of gaseous mixture.

When liquid starts to penetrate into a wood chip, the gas present inside the void spaces becomes compressed. Transport of liquid will then be slowed down and eventually stop because of the growing back-pressure. After pressure equilibrium is achieved, further penetration would be possible either due to an increase in the pressure applied or a decrease in the pressure of the gaseous mixture.

Neglecting the presence of minor gases, the total pressure of the gaseous mixture can be assumed to be the sum of the partial pressures of air and water vapour (*Eq.2*). The last one is a function of temperature and can be considered constant under unchanged conditions. Then, the decrease in gas pressure inside the wood chip could take place only via a reduction in the amount of entrapped air. Theoretically, some air may be pushed out of the chip by the penetrating liquid, which is determined by the geometry of the capillary system. Also, the chemicals present in the penetrating aqueous solution may consume the oxygen contained in the air. In practice, however, the most probable way for remaining air to escape from the chip voids is by dissolution into the surrounding liquid and outward diffusion.

$$P_g = P_a + P_v \tag{2}$$

where

P_g is pressure of gaseous mixture,
P_a partial pressure of air,
P_v partial pressure of water vapour.

The structure of wood and the fact that the cell walls are hydroscopic complicate the mechanism of liquid penetration into the wood chip. A number of different simultaneous phenomena take place when the liquid penetrates into the wood voids. While some phenomena may have a positive effect on the penetration process, others might cause obstruction of the liquid flow. For example, diffusion of water vapour may play a critical role during penetration into dry wood chips [5]. On the other hand, capillary condensation of vapour in pit pores above the penetrating liquids may prevent the escape of entrapped air from the fibre cavities with fine pit openings [12], thus limiting the efficiency of penetration. The effects of bound water, swelling of the cell wall, and surface tension forces at the gas-liquid interfaces within the wood chip on the penetration process are still unclear.

$$U = \frac{K}{\mu}\frac{\Delta P}{L} \tag{3}$$

where

U is velocity of liquid movement,
L length of the specimen,
ΔP pressure differential,
μ dynamic viscosity of liquid,
K specific permeability of wood chip.

Theoretically, different kinds of liquid flow may occur in a porous medium such as wood [13]. The viscous or linear laminar flow is considered to be the dominant one. Viscous flow in a porous medium can be described by Darcy's law (*Eq.3*), which relates the flow rate of fluid of viscosity, μ, directly to the pressure differential and inversely to the length of the specimen [13]. K is the permeability constant, characteristic of the penetrated medium and independent of the penetrating fluid. It is generally expected that true turbulent flow is unlikely to occur in wood capillaries because the critical Reynold's number for a transition from laminar to turbulent flow is much higher than that which can be achieved in most woods [13-15]. However, non-linear flow due to kinetic energy losses can occur in wood, particularly where fluids enter a pit opening [15-17]. Molecular slip flow can be considered insignificant due to relatively short mean free path of liquid molecules.

3.2 Factors affecting the process

A great deal of knowledge has been obtained regarding the factors that influence the penetration of various liquids into wood chips. These factors can be put into three groups (*Figure 4*). The first group includes factors related to wood chips, such as the structure of wood capillaries, chip dimensions, the moisture and air contents of the chips, and the chemical composition of wood. The second group includes factors related to the liquid, such as its viscosity, surface tension, composition, air solubility and air saturation degree. Process conditions, such as pressure, temperature and duration of penetration, form the third group of factors.

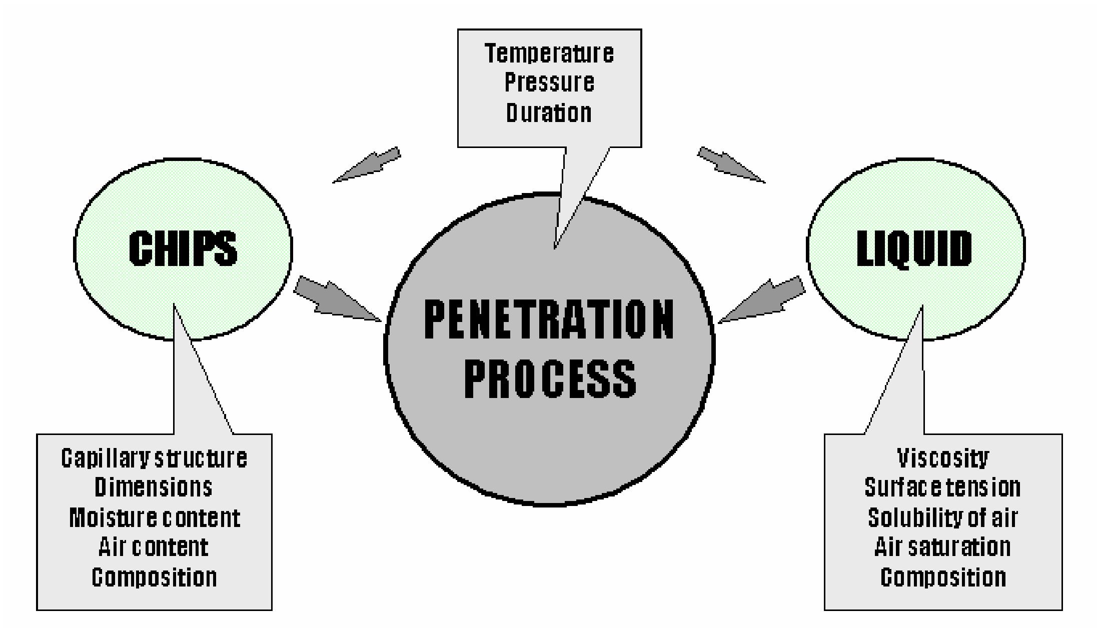

Figure 4. Factors affecting penetration process [I].

3.2.1 Factors related to wood chips

Arguably, the most important factor that affects the penetration is the capillary structure of wood chips. The structure of the wood capillaries, which is defined by their types, geometry, distribution and accessibility, is different in softwoods and hardwoods, sapwood and heartwood, earlywood and latewood, normal wood and reaction wood and also varies between wood species. For example, the penetration efficiency into larch chips is expected to be lower than that into pine and spruce because of the significant differences in capillary structure [18] and a higher density [II].

Figure 5 compares penetration of water into sapwood and heartwood chips [II]. The final penetration degree of sapwood chips is much higher than that of the heartwood chips mainly due to the higher initial moisture content. In contrast to the sapwood chips, the penetration into the heartwood chips is more gradual and the compression level is not easily reached. This can be explained by the difference in the capillary structure of the wood. Obstruction of liquid flow inside the heartwood chips can be caused, for example, by pit aspiration and resinification of interconnecting capillaries [5,19].

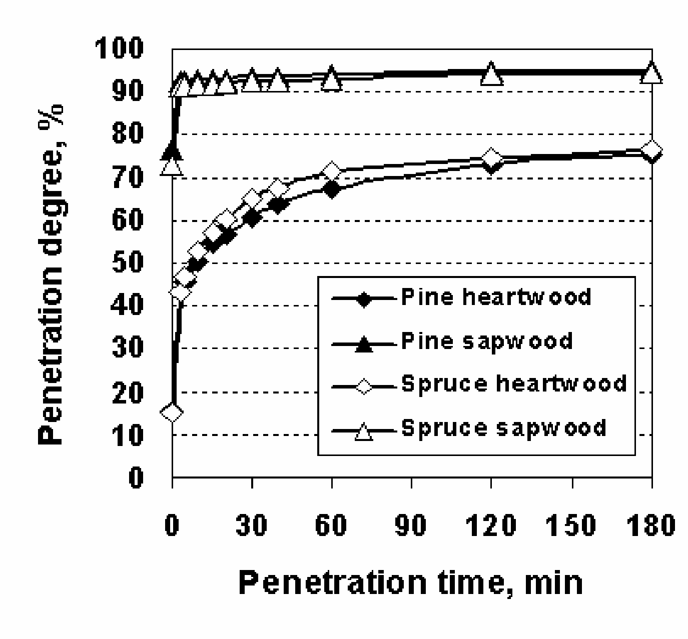

Figure 5. Water penetration into softwood chips: sapwood vs. heartwood [II].
Chip dimensions: 25x15x8 mm. Penetration conditions: temperature 20 ℃, over-pressure 2 bar.

Regarding the capillary structure of a wood chip, it is important to add that the availability of artificial flow paths, such as cracks or fractures, can play an important role for penetration. The rate of liquor penetration into commercial chips may be higher than expected due to the fissured structure of the chips. It has also been suggested that cracks and fissures could be created inside thick chips by various crashing or compressing methods to improve the penetration of liquor [19,20].

A special set of experiments was carried out with the pine heartwood chips to study the effect of chip dimensions on water penetration efficiency [Appendix A]. Data from the experiments were statistically analysed. The regression models obtained were statistically good and had no lack of fit. The analysis indicated that the chip length had a significant effect on the penetration degree. The effects of thickness and width dimensions of the chips were not significant at 95 % confidence level. The effect of chip thickness, however, was more pronounced than that of chip width. These results lead to the conclusion that most of the penetration into pine chips takes place through the longitudinal direction, while radial flow may account for a small part of the total penetration [Appendix A].

This is in good agreement with common knowledge related to the flow in softwood species. The longitudinal flow of liquid takes place via tracheids and interconnecting bordered pits and is expected to be 50-200 times faster than flow in the other two directions [5,11]. Tangential flow in softwoods is controlled by the bordered pits situated on the radial walls of tracheids [21], while the flow in the radial direction is controlled by ray cells [21-23]. The permeability of softwoods in radial direction is considered to be greater than that in tangential direction [21,23].

The permeability of a wood chip is strongly influenced by its moisture and air contents. Excess moisture in the wood voids may have some negative as well as positive influence on the efficiency of penetration [I]. It is generally agreed, however, that the air present within the wood capillaries is the main obstacle to rapid penetration of liquor [23-25]. When penetration is allowed to occur from both sides of the wood chip, the back-pressure of entrapped air, which becomes compressed, soon checks the penetration. For this reason, in order to reach a high penetration degree, it is more favourable to have chips with a higher moisture content and less air.

In addition, the chemical composition of wood chips has a bearing on the penetration process. Phenomena that take place during penetration, including capillary rise, swelling, and chemical interactions are greatly dependent upon the nature of the wood constituents. A high content of extractives, for example, can negatively affect the penetration of liquid by enhancing pit aspiration and plugging capillaries, reducing the wetting of surfaces and decreasing the effect of capillary rise [26], forming a colloidal solution [27].

3.2.2 Factors related to penetrating liquid

The viscosity of the penetrating liquid and the surface tension at the liquid-gas interface are considered as major characteristics influencing the penetration efficiency [5]. Based on Darcy's and Poiseuille's laws [13], the rate of viscous flow of fluid is inversely proportional to its dynamic viscosity. The overall effect of surface tension on the efficiency of liquid penetration into wood chips still remains unclear. On the one hand, high surface tension may improve the penetration efficiency by facilitating capillary rise. On the other hand, high surface tension in the water-air menisci at the narrow pit membrane openings above the penetrating liquid may negatively affect the penetration efficiency by reducing the amount of pores and capillaries available for liquid passage. Still, the effect of surface tension can be expected to be less significant than the effect of the dynamic viscosity of the liquid.

Other factors, such as the solubility of air in the penetrating liquid and the degree of air saturation at the beginning of penetration, determine the efficiency of the latest stages of the penetration process. The chemical composition of the penetrating liquid may affect the penetration process in several ways. Reactions between chemicals present in the penetrating liquor and wood constituents may alter the capillary structure of the chip. Also, the chemicals may consume the entrapped oxygen, causing a decrease in the gaseous pressure inside the chip. In addition, the nature of the liquids has a significant influence on the swelling of the wood [28,29]. Still, it is not well understood how the swelling of wood influences the liquid penetration process [I].

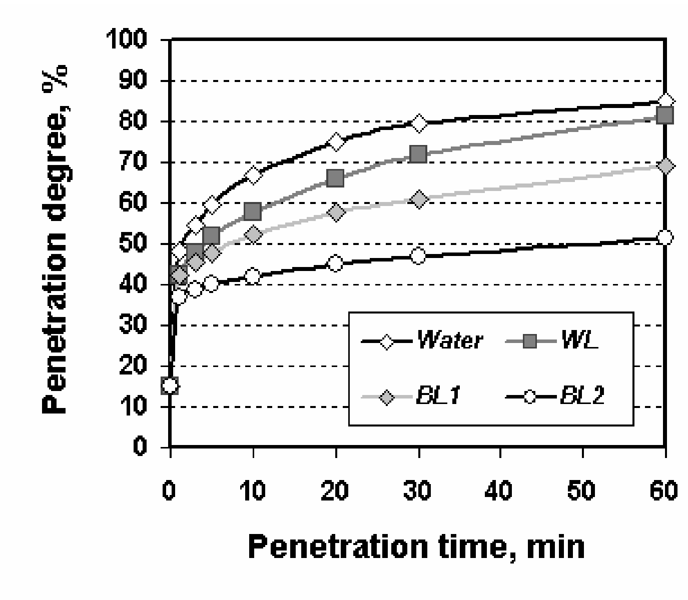

Figure 6. Penetration of water and liquors into pine heartwood chips.
Chip dimensions: 25x15x8 mm. Penetration conditions: temperature 25 ℃, over-pressure 5.3 bar. Liquid properties are listed below [Appendix B]:

	Liquid	*EA, g/l*	*DS, %*	*Viscosity, mPa s*	*Surface tension, mN/m*
WL	*White liquor*	*120*	*10*	*1.95*	*55*
BL1	*Black liquor*	*10*	*10*	*1.44*	*32*
BL2	*Black liquor*	*10*	*21*	*2.51*	*32*
	Water			*0.89*	*72*

Figure 6 compares the penetration of water and cooking liquors into pine heartwood chips [Appendix B]. There is a great difference in penetration efficiency of liquids when compared at the same process conditions. Penetration of water takes place more rapidly than penetration of liquors, which can be primarily explained by lower viscosity. White liquor penetrates into pine heartwood chips faster than the black liquors, although its viscosity is higher than the viscosity of one of the black liquors [Appendix B]. Low surface tension of black liquor may be considered as one of the reasons for slow penetration. It seems, however, that there is another factor limiting the flow of black liquor. The presence of large organic molecules in the black liquor may, for example, limit the penetration efficiency by plugging the small pores and capillaries, thus making them less permeable. The penetration of black liquor with a high dry-solids content (BL2) was the least efficient, which can be attributed to the same phenomenon as well as the highest viscosity among the four liquids.

Based on the 5.3 bar over-pressure and initial penetration degree, the final compression level for penetration into pine heartwood chips would be expected to be around 86 – 88 %. As can be seen from Figure 6, only penetration with water enabled achieving this level within the first hour. Penetration with white and two black liquors resulted in penetration degrees of 81 %, 69 % and 51 %, respectively. This low efficiency of black liquor penetration has to be emphasised when examining contemporary cooking systems. Kraft displacement batch cooking processes and also some modern continuous systems [30] effectively utilize black liquor in the impregnation stage to meet some of the principles of the "modified cooking" concept. The inefficient penetration of black liquor offers plenty of scope for improvement through optimisation of process conditions.

3.2.3 Process conditions

An increase in the process temperature in the range below boiling point under constant pressure was found to increase the rate of liquid penetration, which was attributed to a reduction in liquor viscosity [10,31]. However, the higher temperature may have some negative effects on the penetration, including thermal expansion of the gaseous mixture within the wood chip voids and reduced solubility of air in the liquor. Lower surface tension caused by the higher temperature will also affect the penetration process. In addition, the temperature of penetrating liquid may influence the penetration process by promoting changes within the capillary structure of wood chips [31] and affecting the swelling process [32]. The overall effect of temperature on the penetration of liquid into wood chips would be strongly dependent on the type of wood chips, the liquid and the pressure applied [I,III].

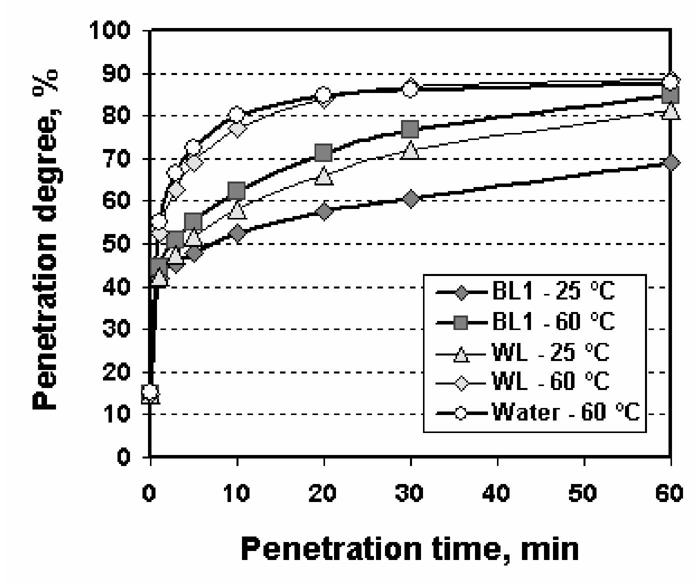

Figure 7. Effect of temperature on penetration of cooking liquors into pine heartwood chips. Chip dimensions: 25x15x8 mm. Penetration over-pressure 5.3 bar. Liquid properties are listed below [Appendix B]:

	Liquid	*EA, g/l*	*DS, %*	*Viscosity, mPa s*		*Surface tension, mN/m*	
WL	*White liquor*	*120*	*10*	*1.95 (25ºC)*	*0.93 (60ºC)*	*55 (25ºC)*	*32 (60ºC)*
BL1	*Black liquor*	*10*	*10*	*1.44 (25ºC)*	*0.71 (60ºC)*	*32 (25ºC)*	*30 (60ºC)*
	Water				*0.47 (60ºC)*		*66 (60ºC)*

Figure 7 shows the effect of temperature on the penetration of cooking liquors into pine heartwood chips [Appendix B]. As can be seen, an increase in temperature greatly improves the efficiency of penetration of both white and black liquors. Apart from its effect on the viscosity of the liquid, higher temperature may also influence the permeability of wood chips. For example, softening the resin compounds present at the pit openings by warm liquor and facilitating chemical interactions between the liquor and wood may increase the effective dimensions of pores [31]. Also, lowering the surface tension in the water-air menisci at the narrow pit membrane openings may improve the penetration efficiency by increasing the number of pores and openings available for liquid flow.

It is interesting to note (Figure 7) that at a process temperature of 60 ºC, the penetration efficiency of white liquor is practically the same as that of water. Still, the difference in viscosity is almost double [Appendix B]. Here, the fast penetration of warm white liquor can be attributed to the effect of temperature on the permeability of wood chips. The rate of chemical reactions between the wood constituents and reactive chemicals present in the white liquor is strongly dependent on the temperature. Thus, some radical changes in the capillary structure of wood chips leading to improved permeability can be expected when the chips are penetrated by white liquor at higher temperature.

It was shown in Paper III that the increase in temperature of the black liquor did not have any noticeable effect on the penetration efficiency into pine sapwood chips. Pine sapwood chips have higher initial moisture content and can be expected to have a better permeability than the heartwood chips. For this reason, the effect of temperature on the penetration efficiency into sapwood chips may be insignificant within some limits.

Since the pressure gradient is a driving force for penetration of liquids into wood chips, it is clear that an increase in the applied pressure will result in faster penetration. In most cases, the application of pressure is a pre-condition for efficient penetration of liquid into wood chips. High enough pressures are required to overcome the negative effect of surface tension in the liquid-air menisci, which are formed by capillary condensation of vapour [12]. Pressure may also affect the capillary structure of wood chips. Because of the plasticity of wood, high pressures may cause stretching and bulging of the pit membranes, thus making the pit membrane openings larger [31]. Higher pressure also results in better solubility of air into the liquid, thus allowing more air to be dissolved and a higher penetration degree to be reached.

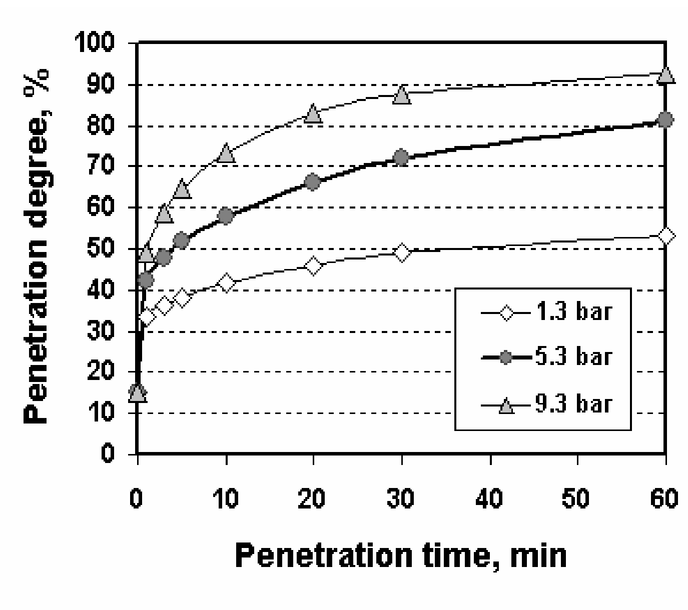

Figure 8. Effect of over-pressure on penetration efficiency of white liquor into pine heartwood chips. Chip dimensions: 25x15x8 mm. Process temperature 25 °C. Properties of white liquor are presented in Appendix B.

Figure 8 shows the effect of applied pressure on the penetration of white liquor into pine heartwood chips [Appendix B]. An increase in applied pressure significantly improves the penetration of white liquor. Higher pressure results in greater air compression, thus enabling a higher penetration degree. The penetration rate is also increased because of the higher pressure gradient and possibly the effect of pressure on the permeability of chips.

The effect of applied pressure is less pronounced for penetration into pine sapwood chips due to the lower amount of air initially present within the chips [III].

The duration of the penetration process is another critical factor that determines the final degree of penetration achieved. Most of the liquid penetration under pressure takes place within a few minutes [24, II, III]. However, the time required to reach the penetration degree corresponding to the compression level strongly depends on the permeability of wood chips and the properties of the liquid. For example, penetration into sapwood chips is usually very rapid, while penetration into heartwood chips is relatively slow [Appendix B, II, III]. As can be seen from Figure 8, 10 minutes was not enough to reach a 60 % penetration degree when penetrating under 5.3 bar over-pressure. Prolonging the time to 30 or 60 minutes resulted in penetration degrees of 72 % and 81 %, respectively. Still, one hour was not enough to reach the penetration degree corresponding to the compression level. The duration is even more important for the latest penetration stage, which is determined by the dissolution of entrapped gas into the surrounding liquid and outward diffusion [31].

3.3 Two cases of penetration: heartwood vs. sapwood

The initial moisture content of wood chips naturally affects the amount of liquid penetrating into the chip voids. Under favourable penetration conditions, this amount may vary significantly between chips with different degrees of initial saturation. Pine heartwood chips with low initial moisture content and pine sapwood chips with high moisture content can be compared in this respect.

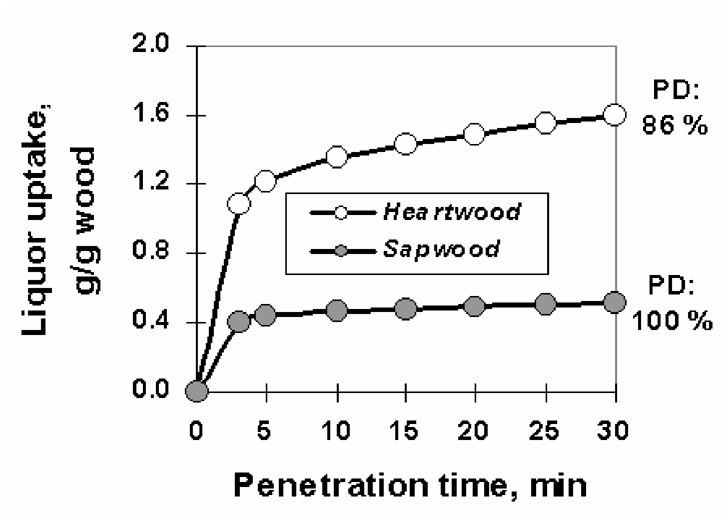

Figure 9. Black liquor uptake into pine chips [III].
Chip dimensions: 25x15x8 mm. Penetration conditions: temperature 80 °C, over-pressure 9 bar.

Figure 9 shows the black liquor uptake into pine heartwood and sapwood chips during penetration at 80 °C temperature and over-pressure of 9 bar [III]. The amount of black liquor that has penetrated into heartwood chips after 30 minutes is almost four times greater than the amount penetrated into sapwood chips. Here, we can speculate about two different penetration cases (Figure 10). During penetration into heartwood chips under high pressure, the air initially present inside the heartwood chip is compressed by penetrated liquor. The fraction of the void volume within the penetrated chip occupied by gases would, of course, depend on the process pressure. For the scenario presented in Figure 10, the gaseous phase within the heartwood chips accounts for 14 % of the void volume. A large part of the remaining volume is occupied by black liquor. At increased temperature, chemical reactions would be expected to take place simultaneously all over the chip, except in the volume occupied by air. This situation would probably cause non-homogeneous cooking with a large amount of rejects.

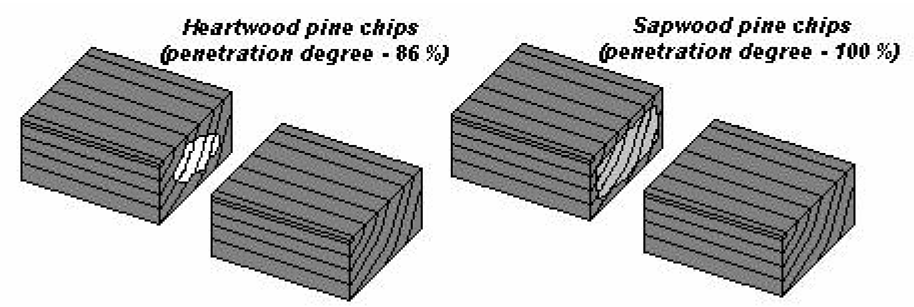

Figure 10. Schematic visualization of two penetration cases: heartwood vs. sapwood. Scenario is based on the results of black liquor penetration experiments [III].

With sapwood chips the situation is completely different, as visualised in Figure 10. The large amount of water initially present within the lumens is pushed towards the chip core, while penetrated black liquor forms a relatively narrow layer. If considering sapwood chips with the properties defined in Paper III, the fraction of black liquor that has penetrated into chip voids would account for about 25 % of the void volume. This fraction may be even smaller during penetration after chip presteaming [III]. Then, the transfer of chemicals into the chip core takes place via diffusion, which is not very efficient at low temperatures. The rate of diffusion of chemicals is slower than the rate of alkaline consumption. Furthermore, with an increased temperature the rate of alkaline consumption will increase relatively more than the diffusion rate [33]. As a result, all the available alkali will be consumed in the chip volume penetrated by liquor. This situation will lead to a significant concentration gradient for alkali within the penetrated sapwood chip. As a result, heterogeneous delignification can be expected: the inner part of the chip will have a higher residual lignin content than the outer part.

In some kraft batch cooking processes with slow heating to cooking temperature, the consequences of the diffusion limitation will not be very dramatic. However, rapid heating, such as in continuous cooking systems, may jeopardise the situation. Then, under conditions of alkaline depletion, undesirable hydrolysis and condensation reactions may take place [34].

It is important to note that the thickness of the wood chips will play a critical role in this case. Thin enough chips could result in a situation where the diffusion limitations are overcome and homogeneous pulping is achieved.

Based on the above discussion, it can be suggested that under front-end conditions that favour efficient penetration, heartwood chips may provide a better result in terms of pulping uniformity than sapwood chips.

4. MODELLING THE PENETRATION OF WATER INTO SOFTWOOD CHIPS

4.1 Introduction

As was mentioned above, it is of vital importance to understand the mechanisms of impregnation and to optimise the process conditions, accordingly. To this end, modelling of the impregnation would be critical for gaining a better understanding of the process. The impregnation model can also be used as a part of the general pulping mode1. An adequate model would provide a quick and inexpensive tool to be used for process control, development of new cooking methods, optimising process conditions and for training purposes.

Several attempts have been made to model various impregnation processes. Quite often the impregnation is considered as a diffusion-reaction process, and complete penetration of chips is assumed [35,36]. Under industrial conditions, however, this assumption can be far from reality; some entrapped air can be expected to be present within the impregnated chips. For this reason, it is important to take into account not only diffusion but also the bulk flow of liquid or penetration when modelling the impregnation process. Some of the suggested models [34,37] deal with the penetration problem by expressing the penetration degree as a negative exponential of the time variable. It can be argued, however, that the “black box” models are too simple and do not provide a clear picture of the process. Zorin [11] and Kimpe [38] have chosen a more fundamental approach. Their impregnation models account for liquor flow into the chips and include the phenomena of capillary rise and air dissolution into the penetrating liquor. To gain a better understanding of the impregnation process and to predict the effect of various factors on its efficiency, it may be advantageous to develop an independent model of liquid penetration into wood chips based on fundamental laws and available experimental data.

In this thesis, the model of the process of water penetration into softwood chips was developed to provide quantitative information on the course of the penetration process under defined conditions. The model describes the process based on fundamental laws combined with some empirical correlations, and therefore can be considered as a “grey box” model. The model development and its applicability for predicting the penetration of water and some cooking liquors are discussed in this chapter. More detailed discussion can be found in Paper VII.

4.2 Model development

4.2.1 Simplifying assumptions

Modelling of a process such as water penetration into wood chips is a difficult task. First of all, the wood substrate is a very non-homogeneous three-phase system. Also, different mechanisms may prevail when the water flows into the anisotropic wood chip from different directions. Second, the penetration process is most likely accompanied by numerous complicated phenomena, including non-linearity of the bulk flow, capillary condensation of vapour and surface tension in the air-liquid menisci, gas dissolution and diffusion, migration of bound water through the cell walls, swelling of wood and other chemical interactions between wood and water. Making certain assumptions may, however, significantly simplify the modelling. To this end, several assumptions were made based on available knowledge [VII] and results from the experiments:

- Wood is a homogeneous porous medium.
- The density of wood substance is constant and equals 1.50 g/cm^3.
- Movement of water into wood chips takes place via the bulk flow under the pressure gradient. Diffusion of bound water and water vapour is not considered.
- Penetrating liquid (water) is homogeneous and incompressible.
- There is no difference in density between bound and free water within the chip.
- Most of the penetration of water into a softwood chip takes place through the longitudinal direction. Radial flow may account for some penetration. However, flow through the tangential direction can be ignored.
- Water flow into wood is laminar and linear.
- Chemical interactions and swelling of the wood chips are ignored. No losses of wood substance occur during liquid penetration.
- Entrapped air escapes from wood voids during the penetration process via dissolution into surrounding liquid and diffusion.

In addition, the whole process of water penetration is considered to be isothermal. So, the amount of air present within the chip at the beginning of penetration is estimated based on ideal gas law under conditions corresponding to the penetration temperature.

4.2.2 One-dimensional model

Because most of the water flow into softwood chips takes place in longitudinal direction, modelling of the penetration, as a one-dimensional process, may be enough for its quantitative description. Considering the cutting pattern of wood chips and assuming the chip to be symmetrical, the half-length of the chip, L_x, can be used in modelling the longitudinal penetration (Figure 11). The objective of modelling is to calculate the fraction of the void volume penetrated by water, ***X(t)***, as a function of time. Moisture initially present within the chip occupies a certain fraction of the void volume, which can be estimated from the known properties of wood chips.

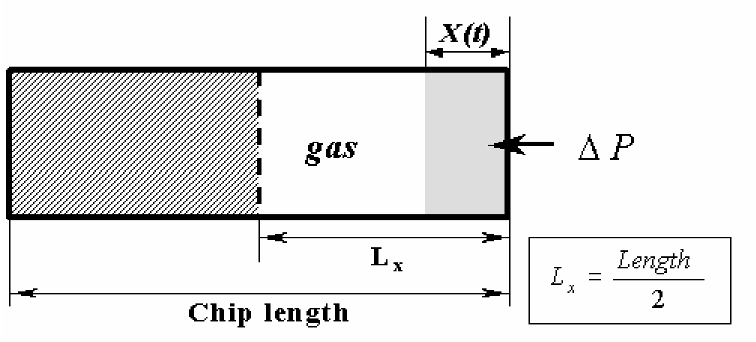

Figure 11. Schematic presentation of longitudinal penetration [VII].

It is known that the flow of an incompressible liquid through a porous medium is described by the equation consisting of viscous and inertial components [39]:

$$\Delta P / L = \alpha \, \mu U + \beta \, \rho_l \, U^2 \qquad \textbf{(4)}$$

where

ΔP	is	pressure differential,
L		length of the specimen,
U		velocity of liquid movement,
μ		dynamic viscosity of liquid,
ρ_l		density of liquid,
α		viscous resistance coefficient,
β		inertial resistance coefficient.

For purely viscous flows, the inertial component is close to zero and can be neglected [39]. Then, by applying the penetration case presented in Figure 11 and assuming that $\boldsymbol{\alpha = K_x^{-1}}$, *Eq.4* can be expressed in the form of *Eq.5*. The formula (*Eq.5*) can be used for calculating the fraction of the chip voids penetrated by water, **X(t)**, as a function of time and known parameters.

$$\Delta P = \frac{\mu}{K_x} L_x^{\ 2} \ X \frac{dX}{dt} \tag{5}$$

where

ΔP	is	pressure differential,
μ		dynamic viscosity of water,
K_x		permeability coefficient of wood chip,
L_x		half-length of the chip,
X		fraction of void volume penetrated by water.

As noted above (see section 3.1), the pressure differential can be considered as the difference between the sum of external pressure, hydrostatic pressure and capillary pressure and the pressure of the gaseous mixture within the chip voids (*Eq.1*). If the presence of some minor gases is neglected, the total pressure of the gaseous mixture can be considered as the sum of partial pressures of air, $\boldsymbol{P_a}$, and water vapour, $\boldsymbol{P_v}$ (*Eq.2*).

$$P_c = \frac{2\gamma \ \cos\varphi}{r} \tag{6}$$

where

P_c	is	capillary pressure,
r		radius of capillary,
γ		surface tension of water,
φ		wetting (contact) angle.

The effect of capillary pressure on the water flow into wood chips is not very clear. Based on experimental results [Appendix C], it was decided to use Jurin's Law (*Eq.6*) [13] for describing the influence of capillary pressure on the water penetration process.

$$\Delta P = \left(P_{ex} + P_h + \frac{2\gamma \ \cos\varphi}{r} \right) - (P_a(t) + P_v) \tag{7}$$

In this case, the pressure differential can be calculated from *Eq.7* based on the parameters that are known or can be estimated from the literature. However, the partial pressure of entrapped air within the chip voids is changing continuously during forced penetration under isothermal conditions: Compression of the gas by penetrating water causes the pressure to increase. At the same time, a slight decrease in pressure takes place due to the dissolution of air into the surrounding liquid. After reaching the compression level, further movement of water would only be possible due to the dissolution of entrapped air into the surrounding water and diffusion towards the chip surfaces.

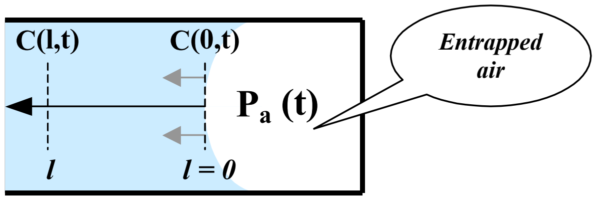

Figure 12. Schematic presentation of dissolution and diffusion of entrapped air.

Figure 12 shows a schematic presentation of entrapped air dissolution and diffusion, which was used for modelling of the process. The amount of the air, $\boldsymbol{n_a(t)}$, dissolved through the unit area of liquid-air interfaces present within the chip can be estimated from *Eq.8*.

$$n_a(t) = A\ D \int_0^t \frac{\partial C(l,t)}{\partial l} \partial t \Big|\ l = 0 \tag{8}$$

where

n_a	is	amount of air escaped from the gas phase through the unit area,
A		parameter that determines the area of phase border,
D		diffusion coefficient of dissolved air in water,
l		distance from the water-gas interface,
$C(l,t)$		air concentration in water as a function of time and coordinate.

The concentration of air in water, $\boldsymbol{C(l,t)}$, as a function of coordinate and time can be found based on the Fick's law for diffusion and Henry´s law for gas solubility (*Eq.9*).

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial l^2} \tag{9}$$

$$\textit{Boundary conditions}: \begin{cases} t = 0 & C = C_0 & l \geq 0 \\ t > 0 & C(0,t) = \dfrac{P_a(t)}{H\,M} & l = 0 \end{cases}$$

where

$P_a(t)$	is partial pressure of air inside the wood chip as a function of time,
H	Henry´s constant,
M	molecular weight of water.

Assuming that air obeys the ideal gas law of state, it is possible to estimate the amount of air trapped inside the wood voids at the beginning of the penetration process. Knowing the initial amount of air and being able to calculate the amount of air dissolved into the liquid phase give us the possibility to estimate the partial pressure of entrapped air, $\boldsymbol{P_a}$**(t)**, at any moment of the penetration process. Zero approximation of the partial pressure of air is determined from the initial amount of air.

4.2.3 Permeability coefficient of wood chips

In Darcy's law for liquids, the specific permeability of the medium is considered as a function of the porous structure of the medium [13]. In this work, however, the permeability coefficient of wood chip, K_x, is considered as a parameter that describes not only the geometry and structure of the wood capillaries, but also other limitations to the flow of liquid.

A special data set obtained from the experiments with water penetration (25 °C) into pine heartwood chips was used to estimate the permeability coefficient of the chips during the course of the penetration process. The results indicate (Figure 13) that the permeability coefficient is directly proportional to the external pressure and inversely proportional to the degree of penetration in the second power.

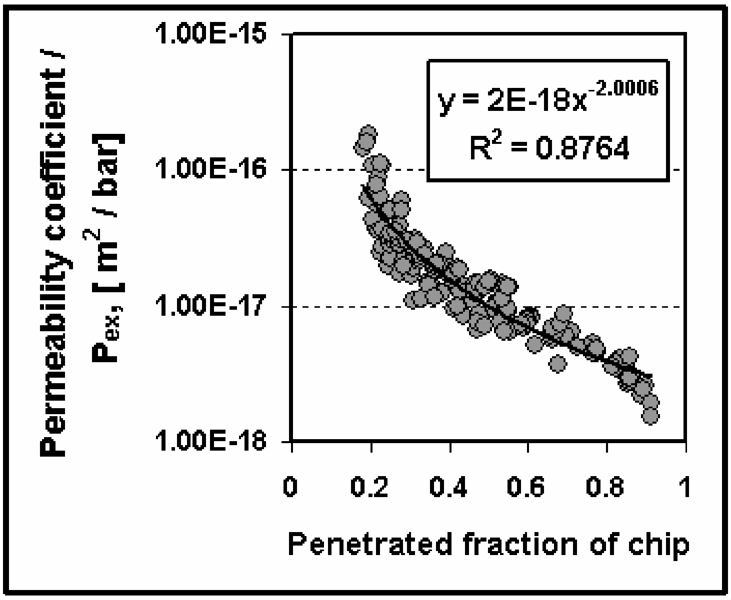

Figure 13. Effect of pressure and penetration degree on permeability coefficient [VII]. Correlation is derived based on the experiments with pine heartwood chips and water at temperature of 25 ºC. Flow of water is assumed to take place only through the longitudinal direction.

The influence of pressure on the permeability coefficient can be explained by the following phenomena. Surface tension in the liquid-air menisci within the narrow pores and capillaries, which are formed due to capillary condensation of vapour [12], may prevent the penetration of water. A high enough pressure differential may be needed to overcome the surface tension in the liquid-air menisci at the narrow pit membrane openings. So, the higher the pressure applied, the greater the number of pores and openings available for liquid passage. In addition, the applied pressure may affect the capillary structure of wood chips (see section 3.2.3).

$$K_x = K_x^{'}\ X^{-2}\ P_{ex} \quad \textbf{(10)}$$

where

K'_x is permeability coefficient, which has to be defined,
P_{ex} external pressure,
X fraction of void volume penetrated by water.

The effect of the penetration degree on the permeability coefficient is probably caused by the same phenomena. During the course of penetration, the pressure of compressed air increases and the pressure gradient drops. As a result of the lower gradient, the surface tension at some narrow openings cannot be overcome. As a result, fewer pores and openings are available for liquid passage, meaning a lower permeability coefficient. The derived empirical dependence (*Eq.10*) is used in the model.

4.2.4 Two-dimensional penetration

Though longitudinal flow is dominant in softwoods, radial flow may still account for a small part of the total penetration, especially if sapwood chips are considered. Consequently, it was decided to include the radial flow in the model. In practice, flows of liquid through the lumens of longitudinal tracheids and via the ray cells cannot be separated due to the presence of interconnecting pits. In this work, however, the radial penetration into a softwood chip is assumed to be independent of the longitudinal one (Figure 14).

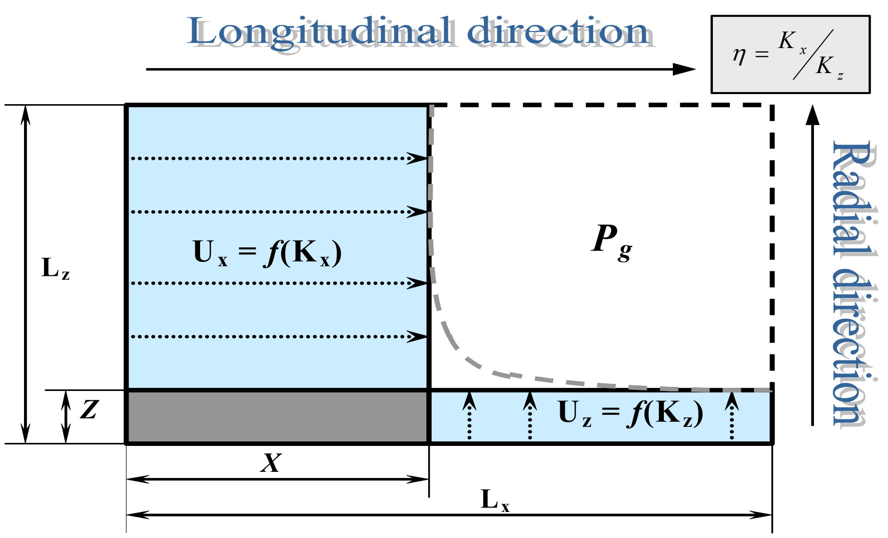

Figure 14. Schematic presentation of two-dimensional penetration [VII].
Liquid penetration into the chip takes place independently from longitudinal and radial directions.
The flow velocities are determined by longitudinal and radial permeability coefficients, $\boldsymbol{K_x}$ and $\boldsymbol{K_z}$.

The total amount of penetrated water at a certain moment is considered as the sum of liquid that has penetrated through the longitudinal direction, $X(t)$, and radial direction, $Z(t)$. The radial permeability coefficient of the wood chip, K_z, is related to the longitudinal coefficient, K_x, through the parameter, η, which can be defined in the range of 50 - 200 [5].

4.2.5 Method of solution

The proposed mathematical model is related to the stiff differential equations that require a special numerical method of solution. The backward differentiation formulas (BDF) were popularised by Gear [40], and are highly effective in solving stiff problems. This method was chosen as a method of numerical solution and acknowledged in all respects.

4.3 Model evaluation

The model extended to two-dimensional penetration case, which is described in sections 4.2.2-4.2.4, was evaluated by comparing the model predictions of different penetration scenarios with the experimental data. Parameters needed for model simulations were set either based on the experimental data (properties of wood chips and penetrating liquid, and process conditions) or the data available in the literature. Permeability coefficient of wood chips (K'_x) was defined as unknown variable that could be adjusted when fitting the simulation results with experimental data. The developed model was first validated against water penetration experiments with pine sapwood and heartwood chips. The influence of air dissolution and outward diffusion on penetration process was also examined based on the model predictions. Finally, the applicability of the model to predict the penetration of cooking liquors was evaluated.

4.3.1 Penetration of water

A comparison of the simulations results with the data from the experiments with pine sapwood chips indicated that the model very closely predicted the penetration of water under different levels of process pressure and temperature [VII]. The defined permeability coefficient for sapwood chips did not have significant influence on the model predictions, when its value was set above $1.0*10^{-16}$ m^2. Pine sapwood chips have a high initial penetration degree of 75 - 80 % and are known to be very permeable. So, it may be impractical to use the sapwood data for testing the penetration model under high pressures. On the other hand, the data collected from liquid penetration into heartwood chips with low initial moisture content may provide better information for evaluating the model.

Figure 15 shows the experimental data and simulation curves for water penetration into pine heartwood chips [VII]. Three penetration cases with different pressures are considered. With the defined permeability coefficient of $1.6*10^{-16}$ m^2, the model enables simulating the penetration of cold water very well.

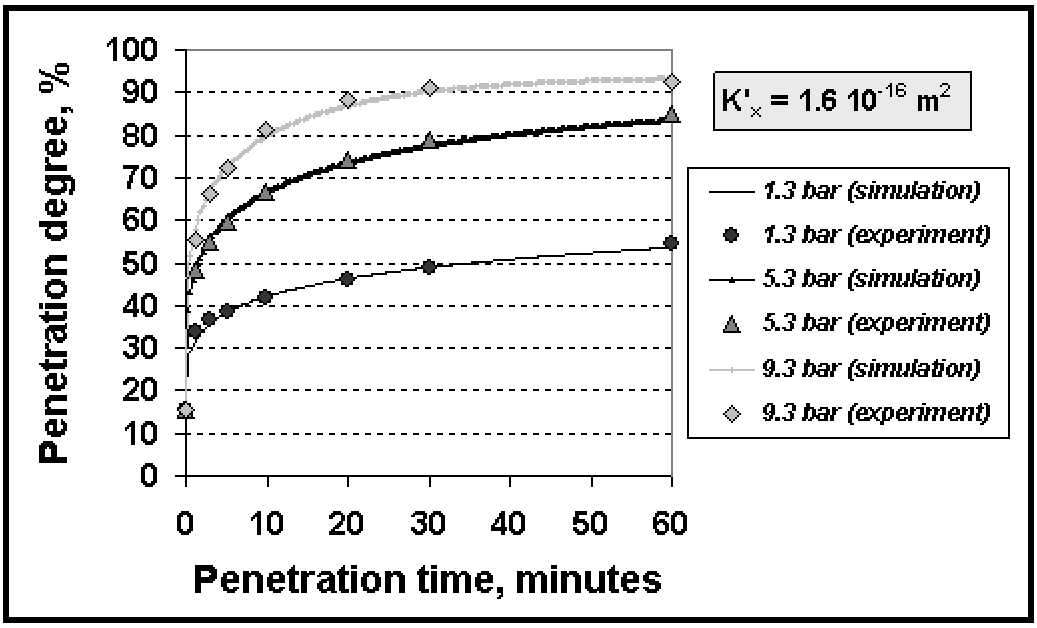

Figure 15. Effect of applied pressure on water penetration into pine heartwood chips [VII]. Process temperature 25 °C. Chip dimensions: 25x15x8 mm. Simulation curves are compared with the experimental data at the same value of longitudinal permeability coefficient, K'_x: $1.6*10^{-16}$ m^2.

Figure 16 compares the experimental data and simulation curves for water penetration at two levels of process temperature: 25 and 60 °C [VII]. As can be seen, the simulation of warm water penetration (60 °C) with the defined permeability coefficient of $1.6*10^{-16}$ m^2 does not describe the experimental data well. However, increase in value of the permeability coefficient up to $2.8*10^{-16}$ m^2 results in an excellent fit between the experimental and simulation data. At higher temperature, this effect is more pronounced, indicating the clear influence of the process temperature on the permeability coefficient of the chips.

As discussed above, a higher temperature may influence the permeability coefficient of chips by lowering the surface tension in the water-air menisci at the narrow pit membrane openings. As a result, more pores and openings will be used by penetrating liquid under the same pressure gradient. Most likely, temperature also affects various interactions between the penetrating water and wood, which can cause changes within the capillary structure of the wood chip. To account for these phenomena, the empirical dependence of the penetrability coefficient on process temperature should be derived based on the available experimental data and then used in the model.

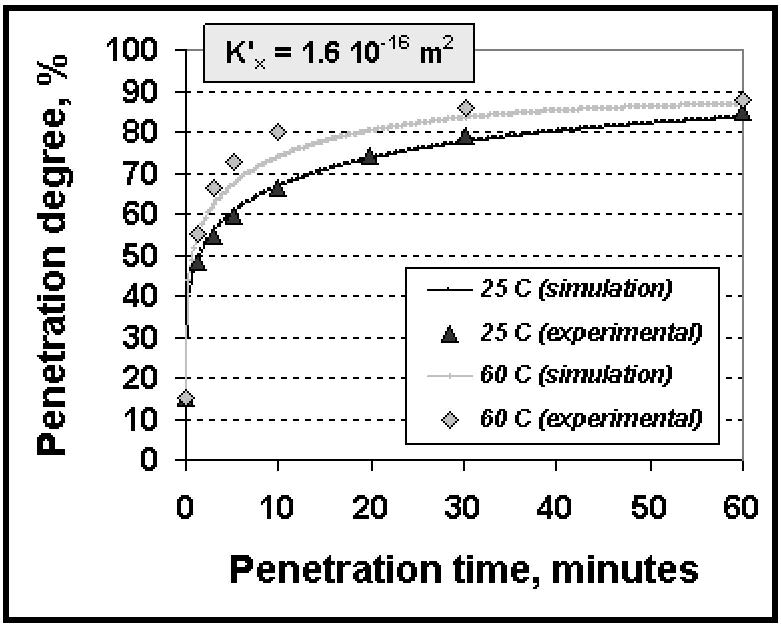

Figure 16. Effect of temperature on water penetration into pine heartwood chips [VII]. Over-pressure: 5.3 bar. Chip dimensions: 25x15x8 mm. Simulation curves are compared with the experimental data at the same value of longitudinal permeability coefficient, K'_x: $1.6*10^{-16}$ m^2.

4.3.2 Effect of air dissolution and diffusion

As was mentioned in section 3.1, escape of entrapped air via dissolution and outward diffusion may play an important role in determining the efficiency of penetration, especially during its later stages. In practice, this process is quite complicated: the gas becomes compressed, while the penetration front moves on, the partial pressures of oxygen and nitrogen increase, the dissolution of these gases proceeds faster, the rate of diffusion of dissolved air changes due to constantly changing concentration differential. Phenomenon of air escape was included into the proposed model through *Eq.8* and *Eq.9*. The Henry's law constant, ***H*** *[bar*(mol_{water}/mol_{air})],* as a function of temperature was estimated based on the data of oxygen and nitrogen solubility in water /39/:

$$H = [(3.3944*0.79 + 2.0156*0.21)\ln T - 2.087]10^4 \qquad bar(mol_{water}/mol_{air}) \qquad \textbf{(11)}$$

A widely used correlation (*Eq.12*) /39/ was used to estimate the diffusion coefficient of dissolved air in water as a function of temperature. The constant was set as 7.7 * 10^{-15} m^2 Pa/K.

$$D(T) = const * \frac{T + 273.15}{\mu(T)} \qquad \textbf{(12)}$$

where

μ is dynamic viscosity of water.

Figure 17 compares experimental data of cold water penetration into pine heartwood chips with two simulation curves: with and without air dissolution. In low pressure case (1.3 bar), the difference between two simulation curves is insignificant. Both curves fit well with experimental data. In high pressure case (9.3 bar), the effect of air dissolution on the penetration efficiency can be observed. However, the difference between two simulation curves becomes clear only after 20 minutes of the process. It seems that simulation of the penetration process that takes into account air dissolution provides better fit with the experimental data.

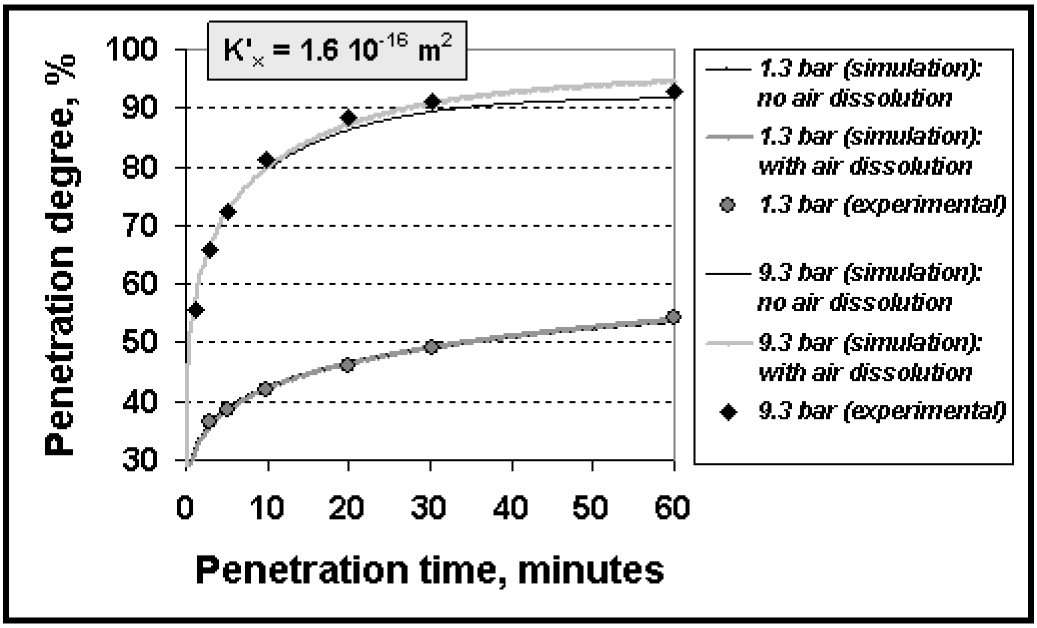

Figure 17. Effect of air dissolution on penetration of cold water (25 ˚C) into pine heartwood chips. Two levels of over-pressure: 1.3 and 9.3 bar. Chip dimensions: 25x15x8 mm. Defined value of the longitudinal permeability coefficient, K'_x, is $1.6*10^{-16}$ m^2.

Figure 18 shows the simulation curves for cold water penetration under high over-pressure into pine sapwood chips. Two cases are compared: with and without air dissolution. Here, the effect of air dissolution on penetration process is more pronounced and becomes obvious already after 5-10 minutes of the process. The experimental data are better predicted by a simulation curve with air dissolution. Ultimately, close to complete penetration of sapwood chips can be achieved, when most of the entrapped gases escape out via dissolution and outward diffusion. Two reasons can be suggested to explain the differences between sapwood and heartwood from the standpoint of air dissolution. First, the amount of entrapped air in sapwood chips is considerably lower than in heartwood chips. Second, the compression level is achieved quite fast in case of sapwood chips due to their high permeability. As a result, the partial pressure of entrapped air, which is compressed by penetrating liquid, reaches its maximum limit also quite fast. Higher partial pressure of air facilitates the dissolution process.

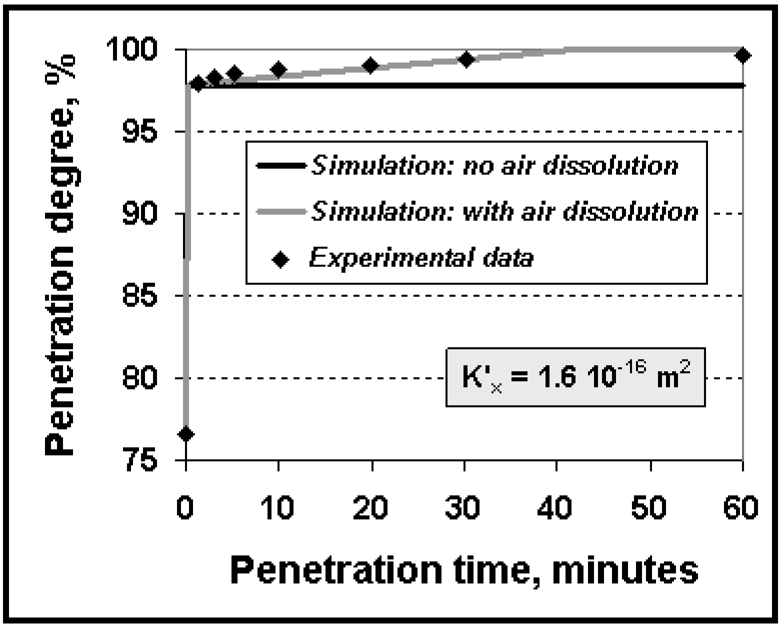

Figure 18. Effect of air dissolution on penetration of cold water (25 ˚C) into pine sapwood chips. Over-pressure: 9.3 bar. Chip dimensions: 25x15x8 mm. Defined value of the longitudinal permeability coefficient, K'_x, is $1.6*10^{-16}$ m^2.

The concept of two-stage penetration process suggested Paranyi and Rabinovitch /31/ can be applied for permeable pine sapwood chips. During primary penetration stage, wood voids are rapidly filled with liquid through the mechanism of mass movement and the compression level is achieved relatively fast. The slow secondary penetration stage is controlled by the dissolution of entrapped gases and outward diffusion. These two stages of the penetration process can be clearly seen from the curves presented in Figure 18.

Figure 19 compares the experimental data of warm water (85 ˚C) penetration into pine heartwood chips with two simulation curves: with and without air dissolution. Here, the penetration process proceeds much faster compared to the case with cold water (Figure 17) and the compression level is reached within 5-10 minutes. Two stages of the penetration process can be distinguished. Again, the simulation curve with air dissolution seems to provide better fit with experimental data. In spite of the fact that solubility of air in warm water (85 ˚C) is about 1.5 times lower compared to the solubility in cold water (25 ˚C), air dissolution phenomenon plays as significant role as in case of cold penetration. This is due to faster diffusion of the dissolved air from wood voids into the bulk solution at higher temperature. Based on this observation, it can be proposed that the process of outward diffusion of dissolved air, not the dissolution process, controls the rate of the secondary penetration stage. The same was suggested by Paranyi and Rabinovitch /31/.

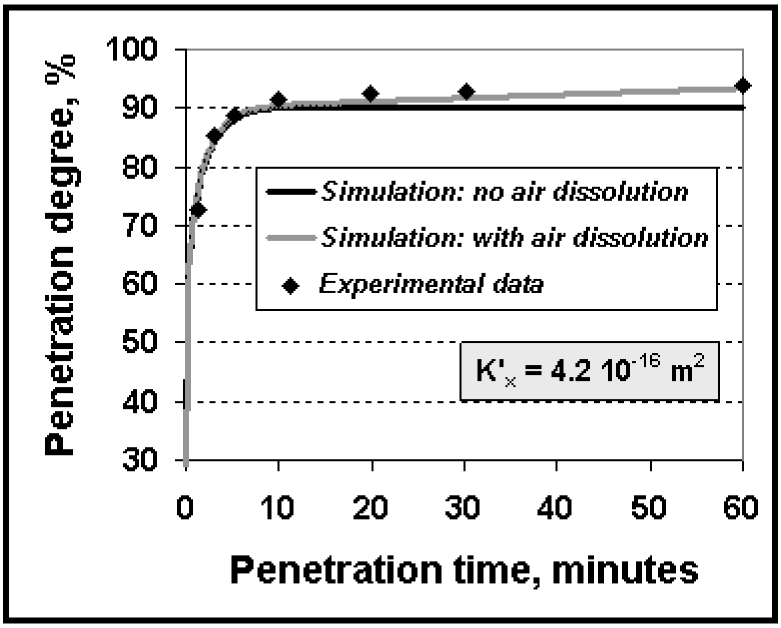

Figure 19. Effect of air dissolution on penetration of warm water (85 ˚C) into pine heartwood chips. Over-pressure: 9.3 bar. Chip dimensions: 25x15x8 mm.
*Defined value of the longitudinal permeability coefficient, K'_x, is 4.2*10 $^{-16}$ m2.*

4.3.3 Penetration of cooking liquors

Corresponding values of the measured properties of white and black liquors, including density, surface tension, and dynamic viscosity [Appendix B], were used in model simulations. The idea was to examine if the change in the basic liquid properties was enough to describe the flow of liquor into chips with the current version of the model.

Figure 20 shows the experimental data and simulation curves for white liquor penetration into pine heartwood chips at two levels of temperature: 25 and 60 °C [VII]. The simulation of white liquor penetration was first carried out with the permeability coefficient of 1.6*10 $^{-16}$ m^2. The simulation of cold liquor penetration (25 °C) is in good agreement with experimental data, when considering the first twenty minutes of the process. After this, the “real” penetration proceeded faster than the simulated one. It is possible that part of the oxygen present in the entrapped air is consumed by reactive chemicals present in the liquor. Thus, higher-than-expected pressure gradients can be achieved in the latest stages of the process. Also, the chemicals present in the penetrating white liquor may affect the chip structure. The current model does not take these phenomena into account.

As can be seen, the defined permeability coefficient of 1.6*10 $^{-16}$ m^2 is too low to simulate the penetration of warm (60 °C) white liquor. Increasing the permeability coefficient to 3.8*10 $^{-16}$ m^2 produces a good fit between the experimental and simulation data (Figure 20) [VII]. Here, the effect of temperature on the permeability coefficient of the chip is quite clear. The rate of chemical reactions between the wood constituents and reactive chemicals present in the white liquor is strongly dependent on the temperature, so a higher permeability coefficient is to be expected when the chips are penetrated by white liquor at higher temperature. In addition, swelling of wood phenomenon may play an important role during the penetration of alkaline liquid, such as white liquor, at higher temperatures. It can be concluded, however, that the suggested model of water penetration can be used for estimating the white liquor penetration. To take into account the increase in the permeability coefficient of wood chips at higher temperature, the additional empirical correlation can be derived and introduced into the model.

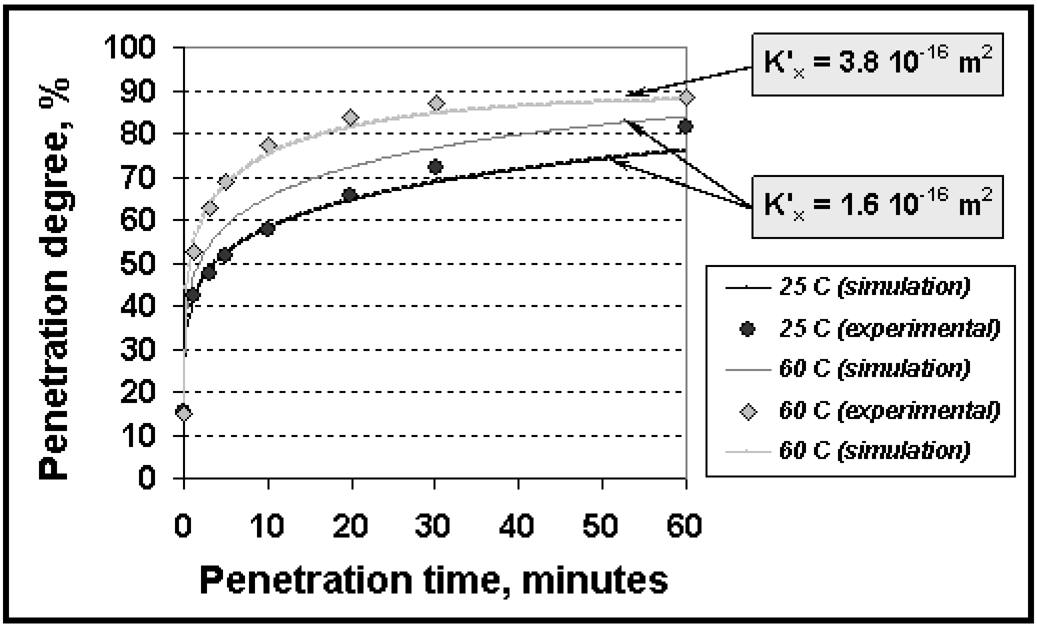

*Figure 20. Effect of temperature on white liquor penetration into pine heartwood chips [VII]. Over-pressure: 5.3 bar. Simulation curves are first compared with the experimental data at the same value of longitudinal permeability coefficient, K'_x: 1.6*10 $^{-16}$ m^2. Simulation of warm (60 ºC) penetration with permeability coefficient of 3.8*10 $^{-16}$ m^2 produces a good fit.*

Figure 21 compares the experimental data and simulation curves for black liquor penetration into pine heartwood chips at two levels of process temperature [VII]. The defined permeability coefficient used in simulations was the same, 1.6*10 $^{-16}$ m^2. As can be seen, there is a significant divergence between the experimental and simulation curves. In this case, the penetration predicted by the model was much faster than the one experimentally observed. Adjusting the permeability coefficient to 0.5*10 $^{-16}$ m^2 enabled predicting the latest stages of black liquor penetration at 25 °C. However, the early stage of the process could not be closely predicted by adjusting the model parameters. The penetration of black liquor at 60 °C was quite closely simulated with the permeability coefficient of 1.0*10 $^{-16}$ m^2.

There are different hypothetical mechanisms that can explain the exceptional behaviour of black liquor. As was discussed in Section 3.2.2, the presence of large organic molecules in the black liquor may have a negative influence on the permeability of the chip by plugging the small pores at the pit membranes. This phenomenon may cause the reduction in the permeability coefficient of wood chips. Indeed, the permeability coefficients used in black liquor simulation ($0.5\text{-}1.0*10^{-16}$ m^2) are considerably lower than those used to simulate the penetration of water and white liquor.

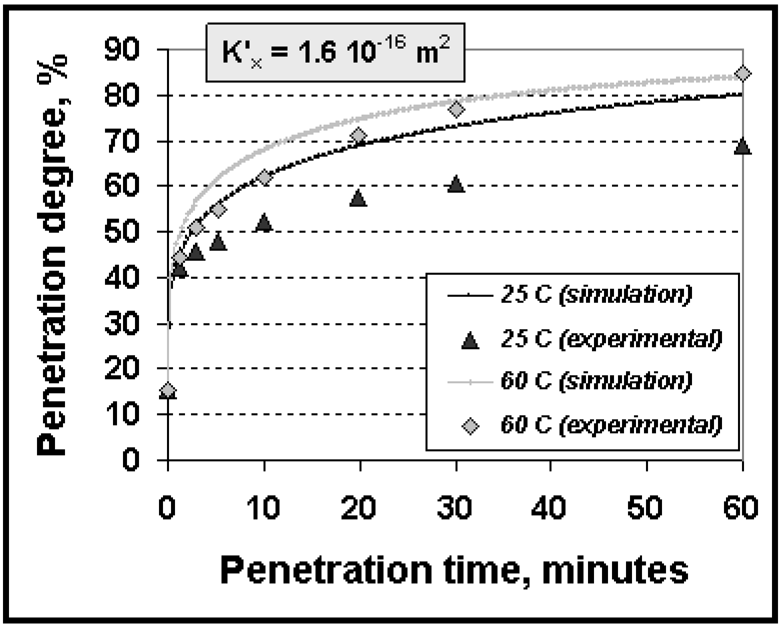

Figure 21. Effect of temperature on black liquor penetration into pine heartwood chips [VII]. Over-pressure: 5.3 bar. Black liquor dry-solids: 11 %. Simulation curves are compared with the experimental data at the same value of longitudinal permeability coefficient, K'_x: $1.6*10^{-16}$ m^2.

It is still unclear, however, why the model is unable to simulate the initial phase of black liquor penetration at low temperature. It can be suggested that black liquor of low temperature may exhibit a non-Newtonian behaviour at the beginning of the penetration process, which cannot be described by the model. Non-Newtonian behaviour is usually expected in highly viscous black liquors at high dry solids content of over 50 % [41]. Based on the calculations suggested for estimating the non-Newtonian flows [41], the flow of black liquor with a dry solids content of 11 % should be Newtonian. However, the black liquor's behaviour at lower dry-solids contents certainly requires more clarification. Testing the penetration of black liquor with 21 % dry solids, for example, indicated that the model could not even be used to simulate warm penetration (60 °C) [VII]. In general, it can be concluded that the current version of the model cannot be used as a general model for predicting the penetration of black liquor. However, it can be used to simulate the penetration of black liquor with low dry-solids content at higher temperature range (60-90 °C).

5. PRESTEAMING OF CHIPS

5.1 Introduction

Much work has been devoted to the development of suitable pre-treatments, in order to improve the penetration of liquids into wood chips. The main objective of these "penetration aid" techniques is to alter the parameters related either to the wood chips or to the liquid, thus affecting the penetration process. Most of the known "penetration aid" techniques can be divided into four groups (Figure 22): "mechanical impact" techniques, addition of surfactants, biological pre-treatments of chips and methods aiming for air removal [I].

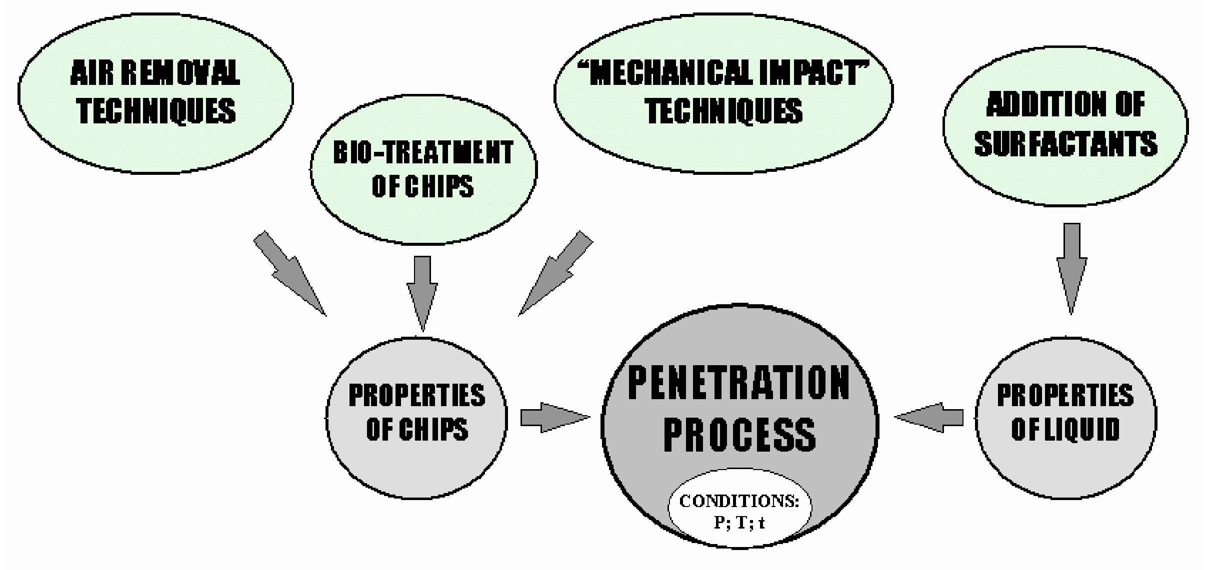

Figure 22. "Penetration aid" techniques [I].

The "mechanical impact" group includes techniques that mechanically affect the structure of wood chips, i.e. inducing cracks and fissures. Addition of surfactants to the penetrating liquid was suggested to improve the penetration through reduction of the contact angle, increased wettability of the wood chip surfaces [42,43], wetting and emulsifying effects on hydrophobic extractives [26]. Several methods have been also suggested based on the biological pre-treatments of chips with enzymes or fungi prior to liquid penetration [44-46]. A number of methods have been developed with the primary aim of removing air from the chips, including evacuation of wood chips and replacement application of condensable gases, such as sulphur dioxide and ammonia [23-25]. The most common technique for air removal is, however, presteaming of the wood chips.

Utilization of steam during the chip charging stage was suggested in the middle of the 1930s [47]. At that time, the main idea behind the use of steam was to achieve uniform packing and to limit the passage of air into the digester. At the beginning of the 1940s, it was shown that presteaming of chips could also improve the impregnation stage in chemical pulping [4]. Because of its effectiveness, relative simplicity and other advantages, steaming of wood chips became a widely used process in the pulp industry. Still, application of presteaming at industrial level allows scope for further development, especially in connection with batch technology. More attention has to be paid to the design of industrial systems to ensure proper contact between steam and chips during a sufficient time interval. In addition, some fundamental issues still require better understanding. For this reason, developing a model of chip presteaming would be particularly important.

Presteaming of chips can serve several functions. It helps to recover heat when flash steam is used [9]. It preheats the wood chips from ambient temperature to 100-120 °C and removes the air between the chips. It also removes the non-condensable gases (NCG), such as air, present in the void volume of the chips [5,48,49]. One can argue that the removal of entrapped air is the most important function from the viewpoint of digester operation and pulping uniformity.

Basically, the main effect of chip presteaming is increase of the temperature within the chip voids. Increased temperature leads to expansion of the air inside the chip voids, accompanied by an increase in the partial pressure of the air. The partial pressure of the water vapour also increases when the temperature rises. The increase in the gaseous pressure inside the chip voids causes the air-vapour mixture to flow towards the chip surface under the pressure gradient. As a result, the air is expelled from the chip. Theoretically, complete removal of air can be achieved when the partial pressure of the water vapour is equal to the ambient pressure. This may be valid, for example, when heating the chips by steam to a temperature above 100 ºC at atmospheric pressure.

In practice, presteaming has to be considered as a simultaneous process of heat and mass transfer inside and outside of the chip. However, it may be advantageous to consider its efficiency from the viewpoint of chip heating and air escape. This may provide a better understanding of the process itself as well as the conditions needed to achieve a certain task. Some speculations and hypotheses related to the efficiencies of chip heating and air escape processes as well as their mechanisms are discussed based on the experimental data and numerical calculations in Paper VI and presented in this chapter.

5.2 Heating-up process

The time needed to heat the chip to the required temperature is an important technological parameter of the steaming process. Only reaching a certain temperature level would give a theoretical possibility for complete air removal from the chips. The efficiency of heating wood chips with steam is affected by a number of factors that can be divided into two groups [VI]. The first group contains the factors related to the wood chip, the second group the factors related to the process. Wood properties such as density, composition, and moisture content determine the heat-conducting properties of the wood chip. The dimensions of the wood chip define the distances for heat transfer. On the other hand, process parameters affect the heating process by determining the rate of heat transferred to the chip surfaces, thus contributing to the efficiency of the entire heating process.

Wood itself is a relatively good insulator [13]. The low thermal conductivity of wood may account for the considerable time interval required to bring the wooden block to a uniform, elevated temperature by application of heat to its external surfaces. Heating of the chip with saturated steam takes place from all three directions. Most of the heat released from the condensation of steam is consumed in the heating process. Calculations show that the heat losses on the evaporation of the water present inside the chips can be ignored. Let us consider "ideal" steaming, where the heat transfer through the liquid film on the chip surface is instantaneous. For a wood chip of parallelepiped shape, anisotropy with orthogonal symmetry can be assumed, where the thermal conductivities are different in three mutually perpendicular directions (axes X, Y, and Z). The heating process of the wood chip can then be modelled based on the fundamental equation for unsteady state conduction in solids and fluids, in which there is no substantial motion [50]:

$$
\begin{aligned}
&\rho_{ch} C_p \frac{\partial \theta}{\partial t} = \lambda_x \frac{\partial^2 \theta}{\partial x^2} + \lambda_y \frac{\partial^2 \theta}{\partial y^2} + \lambda_z \frac{\partial^2 \theta}{\partial z^2} \\
&\text{Boundary conditions:} \\
&\theta \big|_{x=0} = 1; \quad \theta \big|_{y=0} = 1; \quad \theta \big|_{z=0} = 1; \\
&\lambda_x \frac{\partial \theta}{\partial x}\bigg|_{x=L_x} = 0; \quad \lambda_y \frac{\partial \theta}{\partial y}\bigg|_{y=L_y} = 0; \quad \lambda_z \frac{\partial \theta}{\partial z}\bigg|_{z=L_z} = 0 \\
&\text{Initial condition:} \quad \theta \big|_{t=0} = 0
\end{aligned}
\tag{13}
$$

Here, $\boldsymbol{\theta}$ is dimensionless temperature; $\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$ are spatial coordinates; $\boldsymbol{\lambda_x}$, $\boldsymbol{\lambda_y}$, $\boldsymbol{\lambda_z}$ are thermal conductivities of wood in a certain direction; $\boldsymbol{L_x}$, $\boldsymbol{L_y}$, $\boldsymbol{L_z}$ are chip dimensions; $\boldsymbol{t}$ is time; $\boldsymbol{\rho_{ch}}$ is density of the wood chip and $\boldsymbol{C_P}$ is the heat capacity of the wood chip.

By transforming the system of coordinates, it is possible to reduce the solution of the anisotropic problem to the solution of the corresponding isotropic problem. In this case, an analytical solution can be found [51]. The basic properties of the experimental chips, density and moisture content [VI], can be used to calculate the heat capacity and heat conductivities in accordance with the relationships suggested by MacLean [52]. It can be also assumed that thermal conductivity in longitudinal direction is 2.5 times greater than that in radial and tangential directions, as has been shown by Siau [13].

The calculated parameters and defined dimensions of the chips were used to simulate the heating of the pine sapwood and heartwood chips (Figure 23). According to the simulations, the time for heating the pine chips with steam up to steaming temperature is quite short, slightly longer than two minutes. The heating efficiency for sapwood and heartwood pine chips is almost the same. Although the thermal conductivity of "wet" sapwood is higher, the higher density and specific heat capacity counteract its influence. In practice, however, the heating of heartwood chip may proceed faster than predicted by simulation [VI]. Part of the steam can diffuse into chip voids and condense inside the chip. Thus, the distances for heat transfer may become shorter [VI].

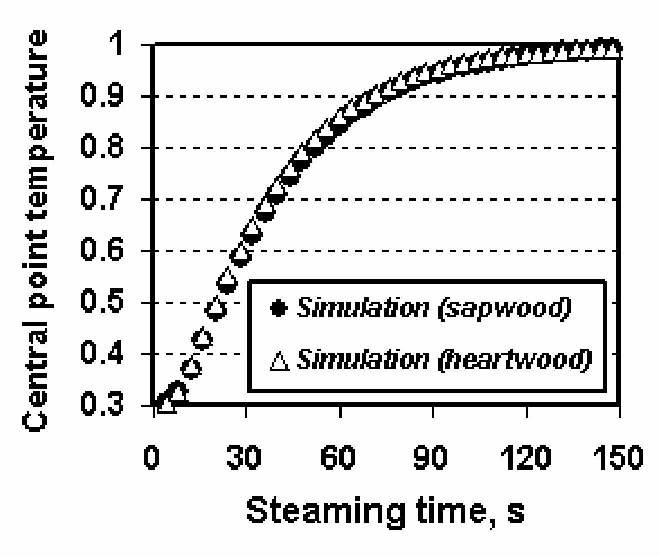

Figure 23. Heating of pine chips by saturated steam of 100 °C [VI].
Starting temperature: 30 °C; Chip dimensions: 25x15x8 mm.

Based on the experimental data and results from simulations it can be concluded that heating of wood chips of typical dimensions with saturated steam is a fast process, lasting only a few minutes. Under industrial conditions, however, longer heating may be expected because of limited heat transfer within the chip layer. Increased chip dimensions, especially thickness, may also result in significantly longer heating times to achieve steaming temperature. Still, fast heating of the wood chips will not guarantee fast air removal.

5.3 Air escape process

Figure 24 shows the effect of presteaming on the penetration of water into pine heartwood chips under 5.3 bar over-pressure. A longer steaming time led to a higher penetration degree, indicating that more air was removed from the chips. A similar effect of presteaming on penetration efficiency was observed with the pine sapwood chips [VI]. Based on the design of the impregnation vessel used, the chip dimensions and the size of the chip sample, it can be assumed that the chip heating process was quite rapid, lasting only a couple of minutes. From the results of the experiments with heartwood chips it seems that the process of air removal takes much longer. In fact, steaming during one hour was long enough to remove most of the air from the chips.

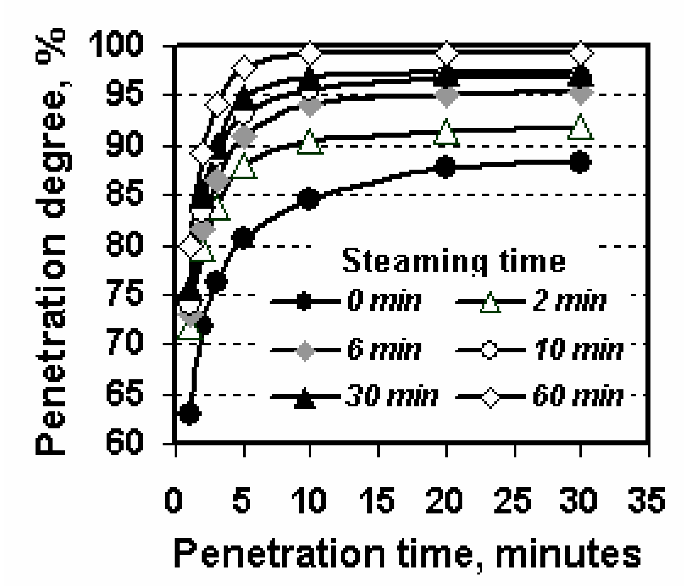

Figure 24. Effect of presteaming on water penetration into pine heartwood chips [VI]. Steaming: 105 °C; Penetration: 85 °C and 5.3 bar; Chip dimensions: 25x15x8 mm.

If the dissolution of remaining air during water penetration into the chips is ignored, it is possible to make a rough estimation of the efficiency of air removal from the chips during presteaming based on the penetration experiments.

$$\frac{\partial N}{\partial t} = -k\,N \tag{14}$$

where

N is amount of entrapped air within the wood chip,
t time,
k proportionality constant.

Figure 25 shows the amount of remaining air as a function of steaming time for heartwood chips. Most of the air is removed during the first two minutes of presteaming, when chip heating takes place. As can be seen, the air escape from the chips during presteaming falls to the negative exponential dependency, *$N = N_0$ exp (-k*t)*. This solution can be obtained from *Eq.14*, where the rate of air escape from the wood chips during presteaming is assumed to be proportional to the amount of entrapped air. The constant *k* is a parameter dependent upon the properties of wood chips.

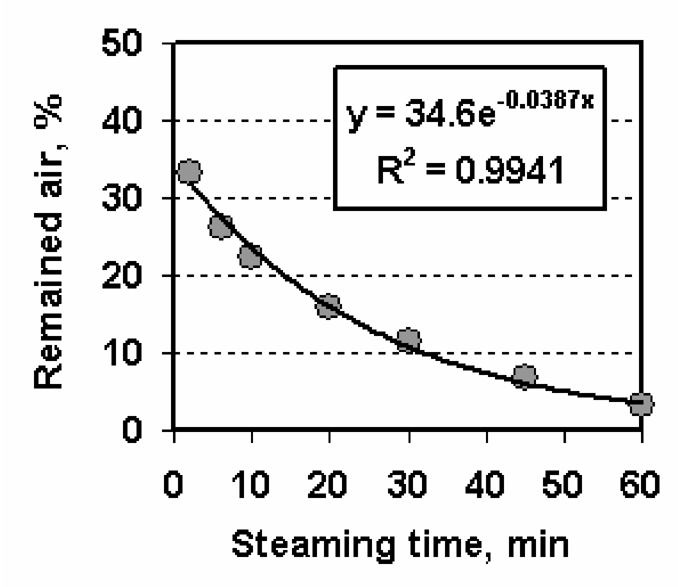

Figure 25. Effect of chip presteaming (105 °C) on air removal from heartwood chips [VI].

To achieve an air removal degree of 90 % for heartwood chips, 30 minutes of steaming was required, while for sapwood chips only 5-6 minutes [VI]. The accuracy of the data presented in Figure 25 was somehow affected by the dissolution of air. Nonetheless, it can provide reasonable information on the efficiency of air removal during chip presteaming. Eventually, the following question arises: What are the mechanisms of air escape from the chips during presteaming and the factors limiting this process?

A gaseous mixture of air and water vapour occupies part of the void volume inside the sapwood and heartwood chips. The increase in temperature that takes place during steaming causes the mixture of air and vapour to flow from the chip voids under the pressure gradient [VI]. Because of the specific features of the capillary structure of softwoods, a flow of gases can be expected to take place primarily in longitudinal direction. Bearing all this in mind, the mass transfer of air from the wood chip, which involves mechanisms of bulk motion and molecular diffusion, can be described in terms of the one-dimensional equation (*Eq.15*) [53].

$$\frac{\partial c}{\partial t} = -\frac{\partial (c,u)}{\partial x} + D_a \frac{\partial^2 c}{\partial x^2} \tag{15}$$

where

c	is	air concentration in gaseous phase,
u		rate of air flow,
D_a		air diffusion coefficient.

Let us consider a case where the wood chip is already heated by steam to its ultimate temperature. Some simplifying assumptions can be made: air is an ideal gas, the gas volume is constant and the process is isothermal. The pressure of the gaseous mixture is the sum of the partial pressures of water vapour and air (*Eq.2)*, where the partial pressure of water vapour, P_v, is constant, so the pressure gradient equals the gradient of the partial pressure of air: $\partial P/\partial x = \partial P_a/\partial x$. The bulk motion of air under the pressure gradient can be described with the help of Darcy's law [13], where the flow rate is related directly to a specific permeability of wood chips to gases and inversely to the dynamic viscosity of air (*Eq.16)*.

$$u = -\frac{K_g}{\mu_a}\frac{\partial P}{\partial x} \tag{16}$$

where

u	is	rate of air flow,
K_g		permeability of wood chip to gases,
μ_a		dynamic viscosity of air.

By applying these assumptions and considering the unsteady-state case, *Eq.15* can be transformed to *Eq.17*. The initial condition for solving this equation can be for example defined as: $P_v = 1$, $P\big|_{t=0} = 1 + 373/298$, while the boundary conditions as $P\big|_{x=1} = 1; \partial P/\partial x\big|_{x=0} = 0$.

$$\frac{\partial P}{\partial t} = \left[\frac{K_g}{\mu_a}\left(\frac{\partial P}{\partial x}\right)^2 + \frac{K_g}{\mu_a}(P-P_v)\frac{\partial^2 P}{\partial x^2}\right] + D_a\frac{\partial^2 P}{\partial x^2} \tag{17}$$

Modelling the process of air escape by means of *Eq.17* and comparing the results of simulations with the experimental data may provide important information about the efficiency of air escape from the chips and the factors limiting this process.

Figure 26 shows the effect of steaming temperature on the subsequent penetration of water into heartwood chips. By increasing the steaming temperature from 105 °C to 120 °C it was possible to achieve a higher final penetration degree. This means that more entrapped air was removed from the chip voids during presteaming under higher temperature. It is probably caused by the effect of temperature on the permeability of wood chip to gases.

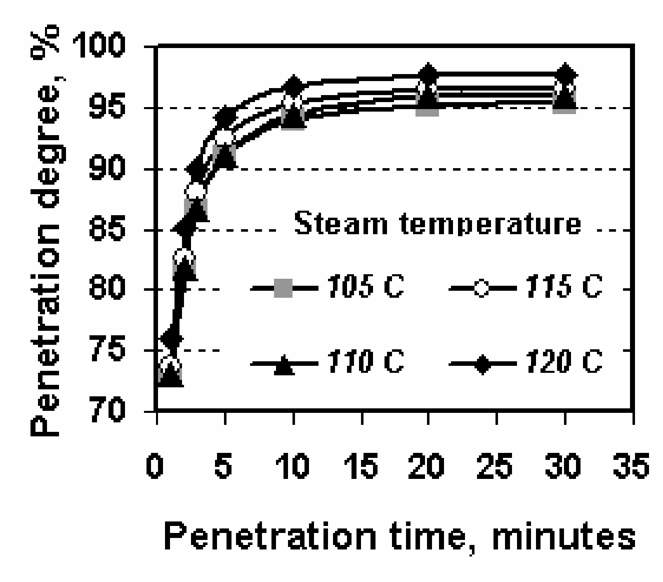

Figure 26. Effect of steaming temperature on water penetration into heartwood chips [VI]. Steaming: 6 minutes; Penetration: 85 °C and 5.3 bar; Chip dimensions: 25x15x8 mm.

Can the entrapped air be removed completely from the chips by presteaming? Extrapolation of the calculated data (Figure 25) shows that to achieve an air removal degree of 99 % for heartwood chips, almost 90 minutes of steaming is required under the conditions in question. In practice, however, complete removal of air may be difficult to achieve, even by applying optimal steaming conditions and long steaming times. The specific features of the wood capillaries can limit the removal of air. Some air cannot be removed because the pressure gradient at the end of presteaming is insufficient to overcome the surface tension forces at the liquid-air menisci that block the air passage. In addition, some air can be trapped within capillaries, which are sealed by extractives, or within the blind pores.

From an industrial point of view, complete removal of air from chips prior to impregnation is desirable, but not vitally important. Prolonged presteaming of chips may not be feasible under industrial conditions. The duration of chip presteaming has to be chosen primarily based on the resources and targets in each particular case. The type of wood chips used and the parameters of the process itself should be also considered when deciding on the duration of chip presteaming.

6. EFFECT OF FRONT-END MODIFICATIONS IN DISPLACEMENT BATCH COOKING

6.1 Introduction

The uniformity of pulping and the ways to improve it have recently attracted a lot of attention. Uniformity of pulping has become a key issue in optimising the performance of digesters. According to current experience, conventional cooking systems do not provide the required uniformity of pulping. Requirements for uniform pulping are well understood, but, unfortunately, not all of them can be met. Some conditions for production of more homogeneous pulp can, however, be fulfilled or strongly influenced. One approach, for example, is to improve wood chip quality either by efficient screening [54-56] or by applying an innovative chipping technique [57] in order to produce high-quality uniform thin chips. Another approach involves application of chip pre-treatments and optimisation of conditions at the front-end of the cook, aiming for improved penetration and efficient diffusion [58,59].

As was shown above, more efficient penetration can be achieved by applying higher process pressure or by using presteaming of the chips. Apart from their positive influence on the impregnation efficiency and pulping uniformity, chip presteaming and higher pressure may also have negative effects. Presteaming, for example, may cause some changes within the lignin structure and complicate its removal [60,61]. It also remains unclear, whether presteaming and better pulping uniformity have any influence on the strength properties of the pulp.

In this thesis work, cooking trials were carried out in order to examine the effect of modified front-end conditions in kraft displacement batch cooking on the cooking performance, pulping uniformity, bleachability and papermaking potential of the pulps. Industrial pine chips were used in cooking simulations. Properties of the pine roundwood used to prepare the chips and the preparation method are discussed in Papers IV-V. The chip samples were cooked in accordance with four scenarios with different front-end conditions, while other cooking conditions were kept constant. Scenario **A** resembled the front-end conditions used in some contemporary industrial kraft displacement batch systems. Three other cooking scenarios included certain modifications, namely a higher-pressure profile (**B**), chip presteaming (**C**), or both (**D**). The remainder of this chapter gives a summary of the main findings from these cooking experiments. A more detailed discussion of the results can be found in Papers IV and V.

6.2 Effect on cooking performance

Yields, rejects and kappa numbers of the pulps from four cooks are compared in Table 1. The amount of rejects and the kappa numbers of the pulps indicate some positive effect of modifying front-end conditions of the cook. Higher pressure and chip presteaming both drastically reduce the amount of rejects; yet, presteaming seems to be more efficient. Also, the average kappa number of the pulp was significantly reduced by the application of either chip presteaming or higher pressure during the hot black liquor stage. The lowest kappa number achieved after cooking scenario D indicates that higher pressure and steaming may have a synergistic influence on the performance of cooking.

Table 1. Basic cooking data [V].

Cooking scenario	A	B	C	D
Screened yield, %	47.5	48.1	47.4	47.1
Rejects, % on wood	1.80	0.30	0.12	0.15
Kappa number	34.4	31.3	31.5	29.5

The effect of modifications can primarily be explained by the improved penetration of liquor into the wood chips during initial cooking stages [II, III]. More thorough penetration reduces the volume within the chips that does not get into contact with chemicals, and shortens diffusion distances. It has also been shown that presteaming of chips may increase the diffusion rate of some ions [62]. These phenomena lead to more uniform distribution of chemicals within the chip when high cooking temperatures are reached. As a result, delignification reactions proceed more uniformly within the wood chips, resulting in less rejects and a lower kappa number for the final pulp.

6.3 Pulping uniformity

Fibre kappa distributions of the pulp samples from cooking scenarios A, C and D are compared in Figure 27. Chip steaming prior to cooking significantly improves the uniformity of pulp. This can be concluded from the narrower kappa distribution and higher percentage of fibres at average kappa. Also, the high-kappa tail present in the pulp sample from scenario A is not seen in the pulp sample from scenario C. Quite similar fibre kappa distribution was obtained for the pulp sample from scenario B, when a high-pressure profile was used but no presteaming of the chips [V]. The pulp sample from cooking scenario D has a slightly narrower distribution and higher percentage of fibres at average kappa. This indicates that chip presteaming improves pulp uniformity even when the chips are cooked with the higher-pressure profile, but the effect is less significant than when cooking with the lower-pressure profile.

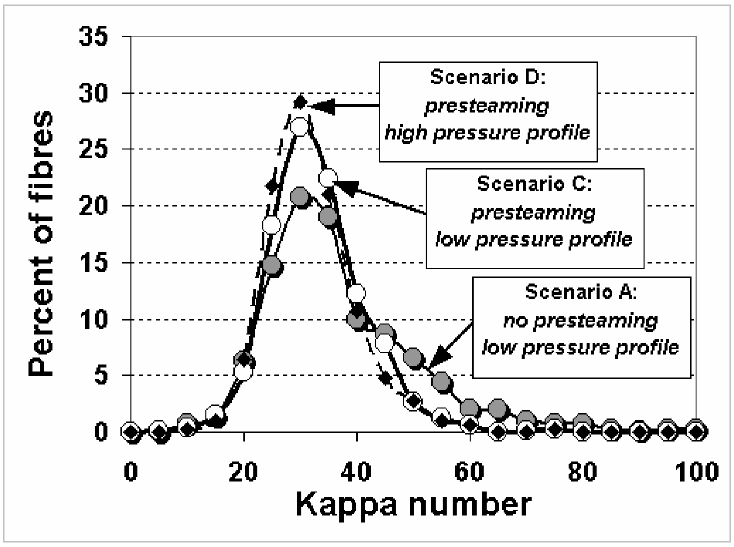

Figure 27. Fibre kappa distributions of the pulp samples from cooking scenarios A, C and D [V] Analyses were performed by using the flow-through fluorescence image analyser [8].

The average values and standard deviations of kappa numbers predicted from the FTIR spectroscopic measurements made on the handmade chips are compared in Table 2. Scenario A resulted in the highest average kappa for both heartwood and sapwood chips. The chips from scenario D seem to have the lowest average kappa number after cooking, while the values for scenarios B and C occupy the intermediate positions. These results show a similar trend as the bulk kappa numbers of the pulps (Table 1).

Table 2. Average values and standard deviations of kappa numbers predicted from FTIR measurements [V].

Cooking scenario	**Average kappa number**		**Standard deviation**	
	Heartwood	***Sapwood***	***Heartwood***	***Sapwood***
A	67.1	56.5	23.9	19.0
B	52.6	48.9	21.4	12.2
C	52.7	50.9	15.3	12.3
D	46.7	46.1	13.2	12.3

It can be noted that there are significant differences in the kappa numbers presented in Table 1 and Table 2. The reason for this is that Table 1 presents the kappa numbers of the bulk pulps produced from industrial chips, while Table 2 presents average kappa numbers predicted from handmade chips. The thickness dimension of the handmade chips was 8 mm, which caused some delignification gradients within the chips (will be discussed below). As a result, the average kappa number obtained for the handmade chips was much higher than the bulk kappa number.

The standard deviation in predicted kappa numbers can be considered as a factor indicating the uniformity of delignification. For heartwood chips, there is a gradual improvement from scenario A to scenario D. For sapwood chips, the highest standard deviation corresponds to scenario A (Table 2). There is no significant difference between the values for scenarios B, C and D. As discussed above, because of the small initial air content in pine sapwood chips, it is enough to apply either slight presteaming of the chips or high pressure to achieve close to complete penetration (see Section 3.2.1). This could be the reason why the application of both chip presteaming and the higher-pressure profile did not further improve the delignification uniformity of sapwood chips.

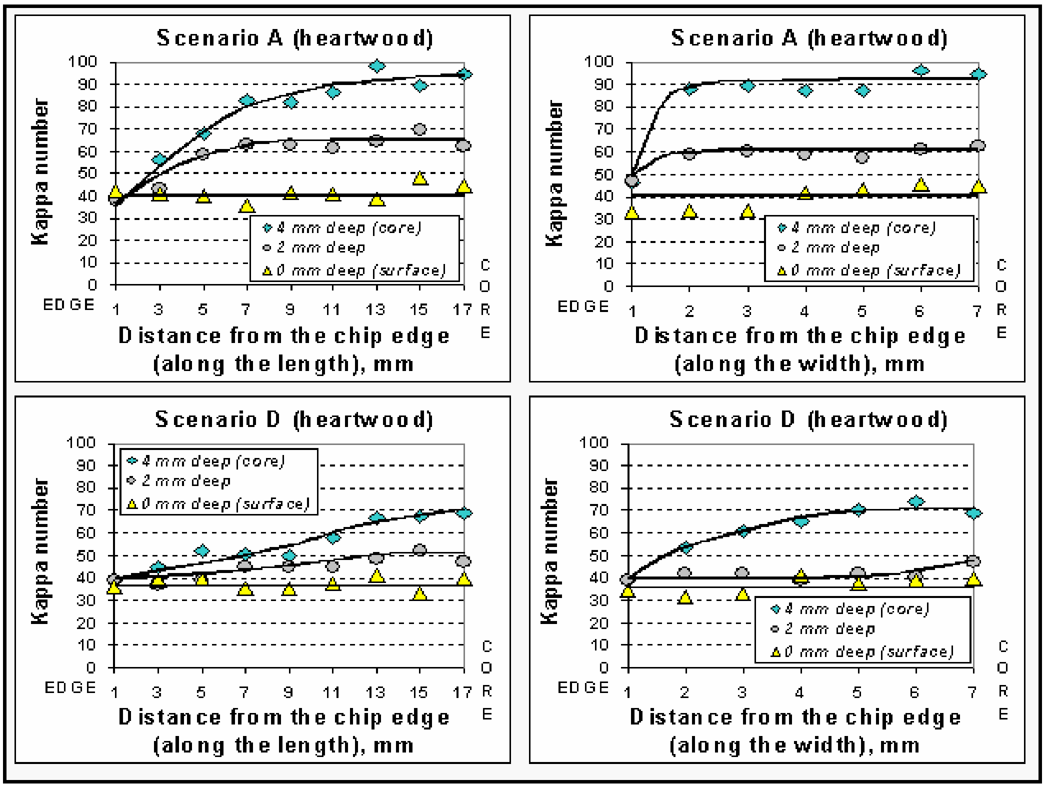

Figure 28. Delignification profiles within the handmade pine heartwood chips [V]. Kappa numbers are predicted based on the FTIR spectral data.

Figure 28 shows delignification profiles within handmade heartwood chips (scenarios A and D) drawn based on the FTIR measurements. It is clearly seen that in cooking scenario A the middle part of the chip (4 mm deep) is undercooked. It is interesting to note that there is a gradual transition along the chip length from the edge kappa number of 40 to the undercooked regions with kappa numbers over 90. At the same time, this transition is very abrupt along the chip width. At a point, which is only 2 mm from the chip edge, the kappa number is already near 90. This may reflect the limitations of mass transfer in the tangential direction in softwoods.

The “2 mm deep” chip layer shows similar trends as the core layer, but within the lower kappa number region of 60-70. As can be seen from the differences between the surface, “2 mm deep” and core layers, there is also a clear gradient of kappa numbers in the radial direction of the wood chip. This emphasises the importance of chip thickness for achieving uniform pulping. In cooking scenario D, the uniformity of delignification of heartwood chips is drastically improved. The “2 mm deep” chip layer has a uniform kappa number profile within the region of 40-50, which is very close to the kappa level of the chip surface. Still, some gradient is present within the middle (“4 mm deep”) layer of the chip. However, the undercooked region is much narrower than in scenario A, and the kappa number level of this region is lower.

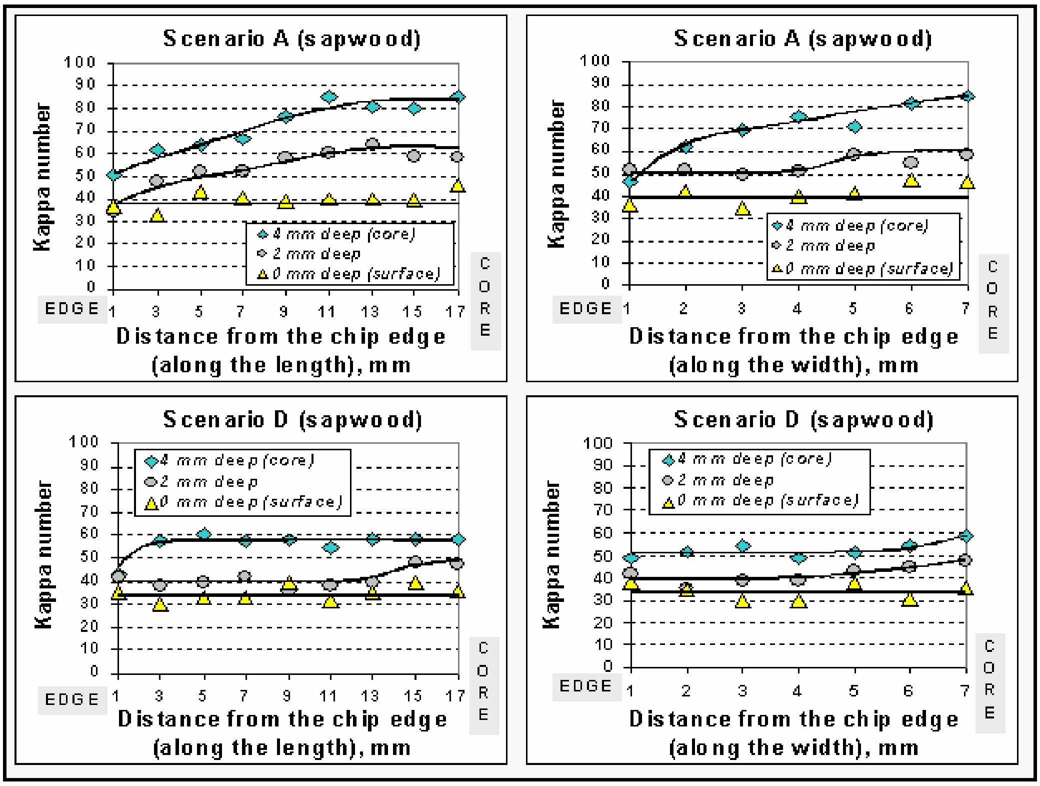

Figure 29. Delignification profiles within the handmade pine sapwood chips [V].
Kappa numbers are predicted based on the FTIR spectral data.

For sapwood chips, a similar behaviour was observed, as shown in Figure 29 [V]. Cooking scenario A resulted in heterogeneous delignification of the sapwood chips, with clear kappa number gradients taking place in longitudinal and radial directions. Application of presteaming and the higher-pressure profile (scenario D) provided more homogeneous delignification with practically no gradients in longitudinal direction. A lower kappa number level was achieved through the whole chip. Still, a slight gradient was present along the thickness dimension of the chip. The effect of pulping modifications on the homogeneity of pulping within the sapwood chips was less pronounced.

We can now return to the discussion in Section 3.3 regarding two penetration cases, heartwood chips versus sapwood chips, and their effect on pulping uniformity. Cooking scenario D can be considered to represent the front-end conditions that favour efficient penetration. Figure 29 indicates that under scenario D, the sapwood chip still has a gradient in kappa number along the radial direction, while practically no gradients in other directions. This may reflect the issue of alkaline depletion discussed in Section 3.3. In the case of heartwood chips (Figure 28), a large proportion of the heartwood chip cooked under scenario D has a very uniform kappa number distribution. The gradient in radial direction is present only in the centre of the chip. This gradient is probably caused by the presence of some air remaining after presteaming or/and some amount of condensate, which were pushed to the chip centre by the penetrating liquor. It is still possible that the conditions of scenario D were not the best ones from the viewpoint of achieving close to complete penetration.

6.4 Bleachability and papermaking potential of pulp

Figure 30 shows the brightness development of the four pulps as a function of chemical consumption. To reach full brightness (88 % ISO), 20 kg more of act. Cl had to be used for pulp A than for D pulp. This difference is important for a pulp producer, when considering the economic and environmental aspects of bleaching. However, when plotting the brightness against the equivalent chlorine multiple there is no differences between the pulps [IV]. It seems that differences in chemical consumption were caused solely by differences in the incoming kappa number of the pulps, not by their bleachabilities. Based on this, the presteaming and higher pressure apparently did not have any significant effect on lignin structure.

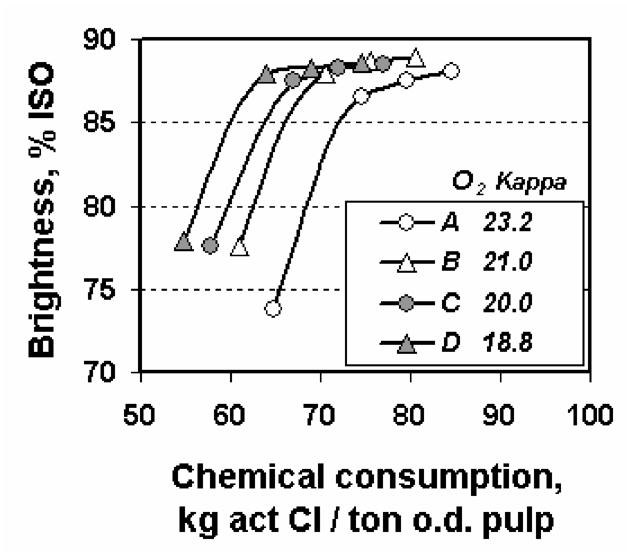

Figure 30. Pulp brightness versus chemical consumption [IV].

Pulp and paper properties were measured from the refined bleached pulp samples of the same brightness (88 % ISO) [IV]. Schopper-Riegler (SR) numbers indicate that the development of dewatering characteristics during PFI refining was very similar for all pulp samples. The light scattering coefficients of refined pulps decrease in a similar manner as a function of sheet density, and when compared at the same sheet density show no difference between the four pulp samples [IV].

The papermaking potential of kraft pulps is largely determined by the quality of the fibres produced in pulping and bleaching operations. Among the important characteristics, physical strength is a unique aspect of kraft pulps, especially for softwood pulp [63]. The strength properties of the four pulps are compared in terms of a strength diagram (Figure 31) that is based on the mean values of the tear and tensile indexes [IV]. The curves indicate that in the tensile index range between 70 and 100 Nm/g, the strength properties of the pulps are almost the same. A comparison of the tear values at different refining levels through standard analysis of variance and the Tukey test showed that none of the pulps differ significantly [IV].

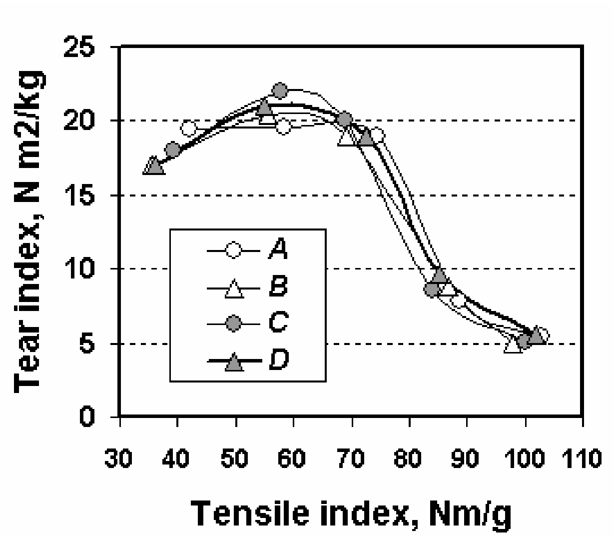

Figure 31. Strength diagram for bleached pulp [IV].
PFI refining at five levels: 0, 500, 1500, 3000, and 6000 revolutions.

The tear - tensile data at various degrees of beating are commonly used as a basis when discussing pulp strength [64]. However, tensile and tear parameters depend on a number of factors, thus resulting in diverging interpretations [65,66]. Measurement of the Pulmac fibre-quality numbers was suggested as an alternative method for evaluating the response of pulps to beating [67]. Comparison of the mean FS number of the pulps, which is the wet zero-span tensile index corrected to the basis weight of 60 g/m^2, at different refining levels showed no significant differences between the pulps [IV].

Table 3. Reinforcement ability (RA) of pulps [IV].

Cooking scenario	A	B	C	D
Fibre length, mm	2.50	2.45	2.46	2.43
Coarseness, mg/m	0.232	0.240	0.243	0.232
Tear index, Nm2/kg (at tensile index of 70 Nm/g)	19.1	19.0	19.9	19.3
Reinforcement ability	202	196	201	202
RA = (length/coarseness) x tear index /68/				

Softwood pulp quality can also be evaluated based on the so-called "reinforcement ability", which should characterise the papermaking potential better than pulp strength alone [68]. A comparison of the reinforcement ability of the four bleached pulps (Table 3) indicates that the papermaking potential of the pulps is practically the same [IV].

7. SUMMARY

A large part of this thesis work has been concerned with examining the penetration efficiency of liquids into softwood chips under various process conditions. To accomplish this task, a novel laboratory impregnator was used. It was found that this device could be successfully used in quantitative studies of liquid penetration into wood chips. The new system can also be used as a tool to investigate the effect of various techniques aiming at improving the efficiency of penetration.

The penetration experiments showed that the efficiency of penetration of cooking liquors is lower than that of water. The viscosity of white liquor is the primary factor determining its slower penetration. At high temperatures, however, the penetration rate of white liquor increases more than can be expected based on the viscosity values. Changes in the capillary structure of wood chips caused by chemical interactions between the wood constituents and reactive chemicals present in the white liquor lead to improved permeability of chips at higher temperature. The slow penetration of black liquor can be explained by the presence of large organic molecules. These large molecules have a negative influence on the permeability of the wood chips by plugging the small pores at the pit membranes, thus making pits less permeable. The penetration efficiency of liquors can be greatly enhanced by applying higher pressure or increasing the process temperature. Also, the application of “penetration aid” techniques, such as chip presteaming has a significant effect on the efficiency of penetration.

It was shown that sapwood chips are more permeable than heartwood chips and that complete penetration can be easily achieved with sapwood chips when applying conditions that favour efficient penetration. However, there is a drastic difference in the amount of penetrated liquor, liquor “up-take”, between the sapwood and heartwood chips. Because of alkali depletion cooking of sapwood chips may still result in heterogeneous delignification. At the same time, heartwood chips may provide more uniform pulping, if the process conditions are optimised to favour efficient penetration.

The experimental data provided a better understanding of the mechanisms of liquid penetration into softwood chips. Based on them, a mathematical model was developed for the process of water penetration into softwood chips under isothermal conditions. The model takes into account several important phenomena, including capillary rise, air dissolution and outward diffusion. A special correlation between the permeability coefficient of wood, process pressure and the chip saturation degree was developed and introduced into the model. The model was found to predict accurately the course and final level of water penetration into sapwood and heartwood chips under defined conditions. The suggested model can also be used for predicting the penetration of the white liquor. However, it cannot be used as a general model for predicting the penetration of black liquor.

Escape of entrapped air via dissolution and outward diffusion plays an important role in determining the penetration efficiency during the later stages of the process, especially when high pressure is applied. The effect of air escape is more pronounced in case of pine sapwood chips, due to lower amount of entrapped air and higher permeability of chips.

Chip presteaming was examined to explore its effect on chip heating and air escape. A three-dimensional model was proposed to estimate the efficiency of heating a single chip by saturated steam. Model simulations and experimental results indicated that the time required to heat a single pine chip with steam was very short, only a few minutes. Under industrial conditions, however, a longer heating time may be expected due to heat transfer limitations. The process of air removal does not proceed as fast as the chip heating process. Based on the experimental data, it was shown that the process of air escape fell to the negative exponential dependency. Achieving a high degree of air removal would require quite long steaming times, up to an hour, especially with "dry" heartwood chips. Complete removal of air, however, may be difficult to achieve, even by applying optimal steaming conditions and long steaming times. The steaming temperature was found to influence the efficiency of air removal, probably by affecting the structure of wood chips. An equation was derived to describe the process of air escape based on the mechanisms of bulk motion and molecular diffusion and is proposed as a model to study the efficiency of air escape from the chips.

The knowledge acquired about the efficiency of penetration and presteaming was applied to the contemporary cooking technology. The effects of improved front-end conditions in kraft displacement batch cooking on the cooking performance, uniformity of pulping, bleachability and papermaking potential of the pulps were examined. Presteaming of the chips and application of a higher-pressure profile at the front-end of displacement batch cooking resulted in reductions in the amount of rejects and kappa number of the bulk pulp as well as improved uniformity of delignification. Application of both modifications simultaneously seemed to provide the biggest effect. According to the results, chip presteaming and higher pressure do not have a significant effect on the bleachability and papermaking potential of pulp. The lower residual lignin content of the cooked pulp and better uniformity in terms of rejects can be used as a trade-off for higher cooking throughput at the same chemical charge and recovery load or reduced bleaching chemical consumption.

8. SUGGESTIONS FOR FUTURE RESEARCH

Many questions still remained unanswered after completion of this thesis work, and more research is needed to achieve a better understanding of the mechanisms of liquid penetration into wood chips. Below are several suggestions for future research topics:

The penetration of cooking liquors into industrial chips needs to be studied. The effect of artificial flow paths, such as cracks or fractures, present within the industrial chips on the penetration efficiency can be examined. Penetration experiments can be carried out with chips prepared from different softwood and hardwood species.

Swelling of wood and its effect on the changes within the capillary structure of the wood chip and the liquid penetration process needs to be understood more deeply. It is also important to get exact quantitative information on the dissolution of wood substances during the impregnation process.

More experimental data are needed to clarify the phenomena related to black liquor penetration into wood chips. Special experiment can be conducted to examine the flow of macromolecules into wood chips. The behaviour of black liquor at low dry-solids contents and low temperatures needs to be explored in more detail.

A special set of cooking experiments with well-penetrated sapwood and heartwood chips can be carried out to compare these two penetration cases from the viewpoint of pulping uniformity.

A lot of scope still remains for improving the suggested penetration model. Some empirical correlations can be derived and included in the model to account for the effect of temperature on the permeability coefficient of wood chips.

The process of air escape from the chips during presteaming requires more attention. A comprehensive model would provide important information about the efficiency of this process and the factors affecting it. To this end, more experimental data are needed to verify the model.

In addition, more effort has to be directed to the research concerning other "penetration aid" techniques, including the use of surface-active additives and bio-treatments of wood chips.

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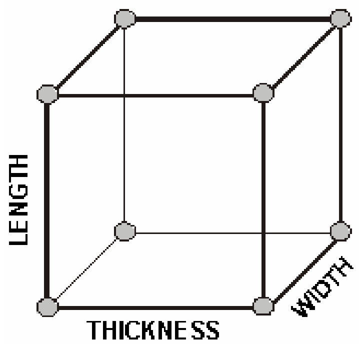
APPENDIX A Effect of chip dimensions on water penetration process

Materials and Methods

Hand-made chips were prepared from the heartwood portion of pine (Pinus silvestris) in exact dimensions. The widths of the chips (tangential direction of the stem) were 5, 10, and 15 mm, and their lengths (longitudinal direction) - 15, 25, and 35 mm, respectively. Their thickness dimensions (radial direction) were 4, 6, and 8 mm. The chips did not contain bark or knots. The moisture content (21 %) and basic density (0.415 g /cm^3) of the chips were determined according to SCAN standards.

Experiments were performed with a specially designed laboratory impregnator at Helsinki University of Technology. A detailed description of the laboratory impregnator and the method can be found elsewhere [1]. The system enables estimation of the penetration degree of wood chips, based on continuous measurements of the chip sample weight throughout the experiment.



	LENGTH mm	WIDTH mm	THICKNESS mm
1	35	5	4
2	35	15	4
3	35	15	8
4	15	15	8
5	35	5	8
6	15	15	4
7	15	5	8
8	15	5	4
9	25	10	6
10	25	10	6
11	25	10	6

Figure A-1. Plackett Burman design for studying the effect of chip dimensions on penetration.

The Plackett Burman experimental design was used to study the effect of chip dimensions on the penetration efficiency (Figure A-1). The penetration trials with water were carried out under 5 bar over-pressure and at two temperature levels of 20 and 75 °C. The penetration degree, as the fraction of the void volume within the chips filled by water, reached after 5 minutes was used as a measured response. Statistical analysis of the data was performed with the Modde 5.0 software package.

Results and discussion

Table A-1. Penetration degree (PD5) of pine heartwood chips after 5 minutes expressed in per cent. Number of experiment corresponds to the number in Plackett Burman design (Figure A-1). Two experimental sets with water, 20 and 75 ℃.

Experiment №		1	2	3	4	5	6	7	8	9	10	11
PD5, %	20 °C	50.7	51.6	51.6	59.4	52.2	60.8	59.4	61.2	54.0	54.7	54.7
	75 °C	77.6	78.7	75.8	84.0	75.9	85.3	85.0	84.7	79.0	78.8	79.5

Penetration degrees of pine heartwood chip after 5 minutes were estimated for two sets of experiments and are listed in Table A-1. The regression analysis was used to fit the experimental data. The ANOVA summaries are shown in Tables A-2 and A-3. Correspondent ***F*** and ***p*** values indicate that fitted regression models are statistically reliable and had no lack of fit.

Table A-2. Analysis of variance (ANOVA) table for experimental set with cold water (20 ℃).

	DF	SS	MS	F	p	SD
Total	11	34019.4	3092.68			
Constant	1	33860.6	33860.6			
Total Corrected	10	158.875	15.8875			3.98591
Regression	3	150.872	50.2908	43.9901	**0.000**	7.0916
Residual	7	8.00261	1.14323			1.06922
Lack of Fit	5	7.67594	1.53519	9.39909	**0.099**	1.23903
Pure Error	2	0.326667	0.163334			0.404146
N = 11	Q2 = 0.813	Cond. no. = 1.0488				
DF = 7	R2 = 0.950	Y-miss = 0				
Comp. = 1	R2 Adj. = 0.928	RSD = 1.0692				

Table A-3. Analysis of variance (ANOVA) table for experimental set with warm water (75 ℃).

	DF	SS	MS	F	p	SD
Total	11	71208.6	6473.51			
Constant	1	71073.6	71073.6			
Total Corrected	10	135.008	13.5008			3.67434
Regression	3	124.985	41.6617	29.0974	**0.000**	6.45459
Residual	7	10.0226	1.4318			1.19658
Lack of Fit	5	9.76261	1.95252	15.0195	**0.064**	1.39733
Pure Error	2	0.259998	0.129999			0.360554
N = 11	Q2 = 0.792	Cond. no. = 1.0488				
DF = 7	R2 = 0.926	Y-miss = 0				
Comp. = 1	R2 Adj. = 0.894	RSD = 1.1966				

Eq.A1 and *Eq.A2* present the regression models for two experimental sets. The analysis indicated that the chip length had a significant effect on the penetration degree when penetrating with water. Its p-values in two experimental sets, water 20 and 75 °C, were 3.7 10^{-5} and 8.6 10^{-6}, respectively. The effects of thickness and width dimensions of the chips were not significant at 95 % confidence level in both experimental sets.

$$\textbf{PD5 (20 °C) = 55.48 – 3.88*Length – 0.01*Width – 0.19*Thickness} \quad \textbf{(A1)}$$

$$\textbf{PD5 (75 °C) = 80.38 – 3.48*Length + 0.06*Width – 0.64*Thickness} \quad \textbf{(A2)}$$

Figures A-2 and A-3 show variable importance in the projection (VIP) plots. The VIP values reflect the importance of the terms (length, width, and thickness) in the model with respect to response (penetration degree). A higher VIP value corresponds to a more significant effect of the factor. As can be seen, the effect of chip thickness is more pronounced than that of chip width. It also seems that the thickness dimension of the chips influences the overall penetration efficiency more when penetrating at higher temperature.

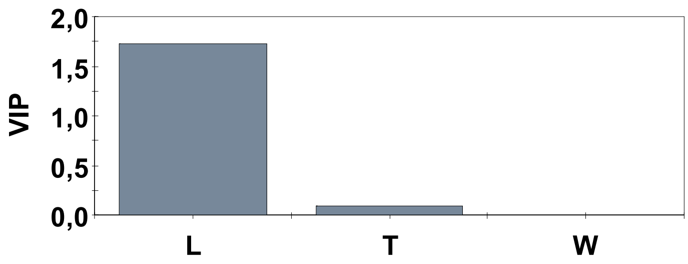


Figure A-2. Variable importance plot for experimental set with cold water (20 °C). (L – chip length, T – chip thickness, W – chip width)

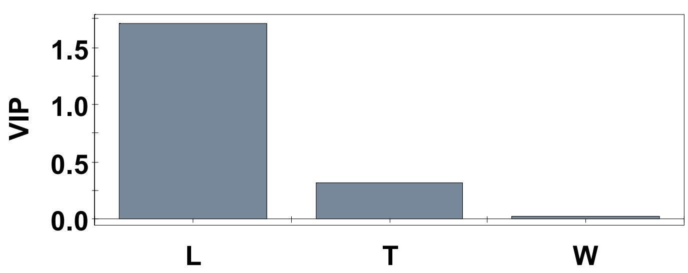


Figure A-3. Variable importance plot for experimental set with warm water (75 °C). (L – chip length, T – chip thickness, W – chip width)

The results lead to the conclusion that most of the penetration into pine chips takes place through the longitudinal direction. Radial flow may account for a small part of the total penetration, while the flow in tangential direction can be neglected. These results are in good agreement with a common knowledge related to the flow in softwood species. The longitudinal flow of liquid takes place via tracheids and interconnecting bordered pits, and is expected to be 50-200 times faster than the flow in the other two directions [2]. The tangential flow in softwoods is controlled by the bordered pits situated on the radial walls of tracheids [3], while the flow in the radial direction is controlled by ray cells [3,4]. The permeability of softwoods in radial direction is considered to be greater than that in tangential direction [3]. Higher temperature of penetrating water may result in softening of the extractives in the ray cells, thus making them more permeable [4]. As a result, enhanced penetration in radial direction can be expected.

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APPENDIX B Penetration of cooking liquors

(Results of penetration experiments with white and black liquors)

Materials and Methods

Hand-made chips were prepared from the heartwood portion of pine (*Pinus silvestris*) in the following exact dimensions: length - 25 mm, width - 15 mm, and thickness - 8 mm. The length of the chips corresponded to the longitudinal direction of the stem, the width and thickness to the tangential and radial directions, respectively. The chips did not contain bark or knots. The moisture content (21 %) and basic density (0.415 g /cm^3) of the chips were determined according to SCAN standards.

Chip samples were subjected to penetration by white and two black liquors at several levels of process temperature and pressure. Cooking liquors were delivered from Metsä Botnia's Rauma Mill, Finland. Their properties were measured within the temperature range used in the experiments. The dynamic viscosity of liquors was measured by capillary viscometry. A viscosity Measuring Unit AVS 350 equipped with thermistor sensors at the measuring levels was used. Surface tension was measured with a KSV Sigma 70 tensiometer by using Du-Nouy ring. The applied force was measured using an electro-balance. The density of the liquors was determined by straightforward measurement of volume and weight. Table B-1 compares basic properties of the liquors with those of process water [1,2] at several temperatures.

Table B-1. Properties of water, white and black liquors compared at several temperature levels.

Liquid	Water [1,2]			White liquor			BL1		BL2	
EA, g/l as NaOH	-			120			10		10	
Dry-solids content, %	-			20			11		21	
Temperature, ºC	25	60	80	25	60	80	25	60	25	60
Dynamic viscosity, mPa s	0.89	0.47	0.36	1.95	0.93	0.61	1.44	0.71	2.51	1.19
Surface tension, mN/m	72	66	63	55	32	-	32	30	32	30
Density, kg/m^3	996	983	972	1167	1152	1145	1062	1045	1119	1100

Experiments were performed with a specially designed laboratory impregnator at Helsinki University of Technology. A detailed description of the laboratory impregnator and the method can be found elsewhere [3]. The system enables estimation of the penetration degree of wood chips, based on continuous measurements of the chip sample weight throughout the experiment. The penetration degree was estimated as the fraction of the void volume within the chips filled by liquid.

Results and discussion

The results of the penetration experiments with cooking liquors and water are presented in Table B-2. As can be seen, there is a great difference in penetration efficiency between water and cooking liquors when compared at the same process conditions (Figure B-1). Water penetrates much faster, which is probably caused by the differences in viscosity and surface tension values. The viscosity of penetrating liquid is considered to be one of the main factors influencing liquid flow through wood capillaries. Also, greater surface tension may result in faster liquor uptake by the capillary forces during the initial penetration. It is interesting to note that black liquor with lower viscosity (BL1) penetrates into pine heartwood chips much slower than the white liquor. It seems that there is an obstruction to the flow of black liquor. The presence of large organic molecules in the black liquor may limit the penetration efficiency by plugging the small pores and capillaries, thus making them impermeable. The penetration of black liquor with a high dry-solids content (BL2) was the least efficient, which can be explained by the same phenomenon as well as the highest viscosity among the four liquids.

Table B-2. Penetration degree of pine heartwood chips (%) as a function of penetration time. Several penetration scenarios with water, white and black liquors are compared.

Liquid	**T, ºC**	**Pressure, bar**	**Penetration time, min**							
			0	1	3	5	10	20	30	60
Water	25	1.3	**15.3**	**34.1**	**36.8**	**38.7**	**41.8**	**45.9**	**49.0**	**54.6**
Water	25	5.3	**15.2**	**48.2**	**54.7**	**59.4**	**66.8**	**74.9**	**79.5**	**85.1**
Water	25	9.3	**15.1**	**56.0**	**66.2**	**72.4**	**81.0**	**87.8**	**90.8**	**92.2**
Water	60	5.3	**15.3**	**55.0**	**66.4**	**72.5**	**80.2**	**84.6**	**86.2**	**87.9**
Water	80	5.3	**15.1**	**62.7**	**75.8**	**80.4**	**84.2**	**87.4**	**88.1**	**88.5**
WL	25	1.3	**15.0**	**33.6**	**36.3**	**38.3**	**41.8**	**46.0**	**49.1**	**53.2**
WL	25	5.3	**15.0**	**42.4**	**47.6**	**51.8**	**57.9**	**66.1**	**71.9**	**81.3**
WL	25	9.3	**15.0**	**49.3**	**58.9**	**64.5**	**73.6**	**82.8**	**87.7**	**92.8**
WL	60	5.3	**15.0**	**52.6**	**62.9**	**69.0**	**77.3**	**83.9**	**87.0**	**88.5**
WL	80	5.3	**15.0**	**55.6**	**66.9**	**73.6**	**81.1**	**86.8**	**88.7**	**90.6**
BL1	25	5.3	**15.0**	**42.1**	**45.5**	**47.8**	**52.4**	**57.6**	**60.8**	**69.0**
BL1	60	5.3	**15.0**	**44.4**	**51.0**	**54.9**	**62.1**	**71.2**	**76.9**	**84.6**
BL2	25	5.3	**15.0**	**36.7**	**38.8**	**40.0**	**41.8**	**45.0**	**46.8**	**51.4**
BL2	60	5.3	**15.0**	**38.8**	**43.5**	**46.2**	**51.0**	**56.8**	**60.6**	**69.0**

The effect of process pressure on the penetration efficiency of white liquor is quite clear. Temperature also has a significant influence, as can be seen from Figure B-2. Apart from decreasing the viscosity of liquid, temperature may also affect the permeability of chips. For example, softening the resin compounds present at the pit openings by warm liquor and certain chemical interactions between the liquor and wood facilitated by higher temperature may increase the effective dimensions of pores.

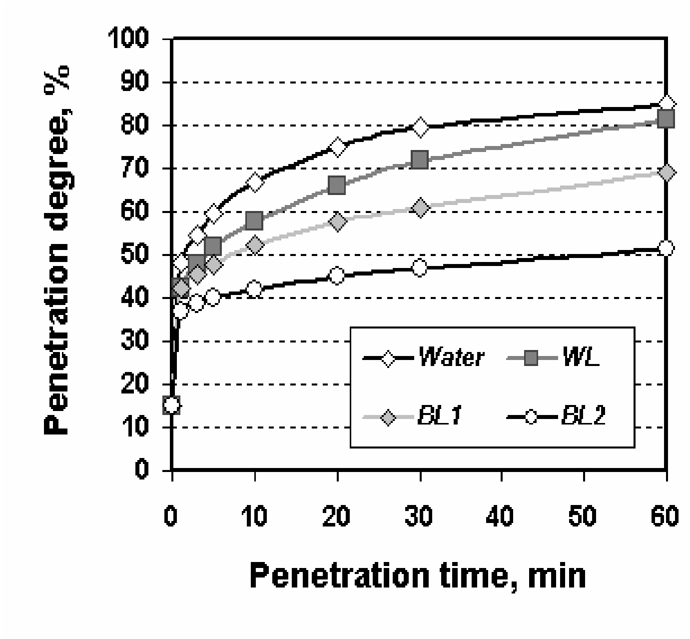

Figure B-1. Liquid penetration into pine heartwood chips. Chip dimensions 25x15x8 mm. Penetration conditions: temperature 25 ℃, over-pressure 5.3 bar.

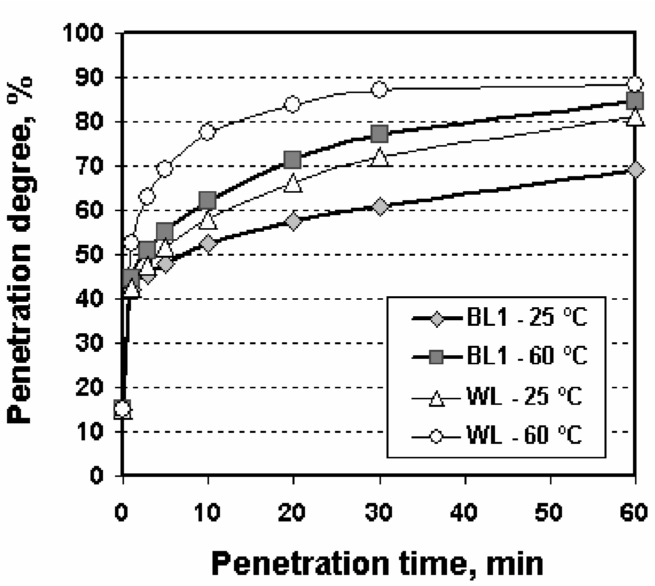

Figure B-2. Effect of temperature on penetration of white and black liquors into pine heartwood chips. Chip dimensions 25x15x8 mm. Over-pressure 5.3 bar.

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APPENDIX C Phenomenon of capillary rise

(Studies on water penetration into the pine chips with no over-pressure)

Materials and Methods

Hand-made chips were separately prepared from the heartwood and sapwood portions of pine (*Pinus silvestris*) logs in the following exact dimensions: lengths - 15, 25, and 35 mm, width - 15 mm, and thickness - 8 mm. The length of the chips corresponded to the longitudinal direction of the stem, the width and thickness to the tangential and radial directions, respectively. The chips did not contain bark or knots. The moisture content and basic density of sapwood and heartwood chips were determined with standard methods SCAN-CM 39:94 and SCAN-CM 43:89 (Table C-1).

Table C-1. Properties of pine chips.

	Heartwood	***Sapwood***
Basic density, g /cm^3	0.415	0.430
Moisture content, %	21	56

Penetration experiments with water at a temperature of 20 °C and no over-pressure were carried out to estimate the significance of capillary pressure for the liquid penetration into heartwood and sapwood pine chips. Experiments were performed with a specially designed laboratory impregnator at Helsinki University of Technology. A detailed description of the laboratory impregnator and the method can be found elsewhere [1]. The system enables estimation of the penetration degree of wood chips, based on continuous measurements of the chip sample weight throughout the experiment. The penetration degree was estimated as the fraction of the void volume within the chips filled by water.

Results and discussion

The effect of capillary pressure on the water flow into wood chips is not very clear. Studies of wood drying have shown that the moisture content of the wood has a drastic effect on capillary pressure [2,3]. Spolek and Plumb [3] suggested the equation for predicting the capillary pressure, P_c [bar], in softwoods as a function of the wood saturation degree (*Eq.C1*). However, this relationship may be inappropriate for the penetration process. For heartwood chips with an initial saturation degree of 0.15, for example, the capillary pressure calculated based on *Eq.C1* is about 4 bar. As a result, a significant capillary rise would be expected after the chips come into contact with water.

$$P_c = 1.24 * 10^5 \left(V_{water} / V_{voids} \right)^{-0.61} \quad \textbf{(C1)}$$

Figure C-1 shows the average values and 95 % confidence interval obtained from the penetration experiments. As can be seen, cold water penetrates the pine chips to some extent at the very beginning of the process. Then, if considering short times – one hour or less, the degree of penetration does not change significantly. Assuming that the capillary pressure is a driving force and that pressure equilibrium is achieved after the initial penetration, the value of the capillary pressure can be estimated from experimental data.

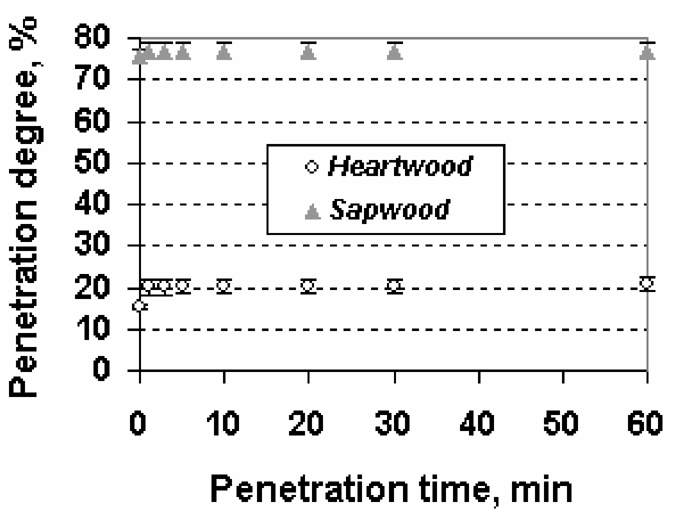

Figure C-1. Penetration of cold water (20 ºC) into pine chips with no over-pressure applied. Chip dimensions: 25x15x8 mm.

$$P_c = \frac{2\gamma \cos\varphi}{r} \quad \textbf{(C2)}$$

Based on the Jurin's Law (*Eq.C2*), the capillary pressure is defined as a function of surface tension, γ, contact angle, φ and capillary radius, r [4]. Of course, the geometry of the capillaries significantly varies within the single softwood chip, resulting in different values of capillary pressure. In can be assumed, however, that the penetration into pine chips would primarily take place through the lumens of the tracheids with the typical radius of 10-15 µm [4,5]. Knowing the surface tension of water (73 dyne/cm at 20 °C) and assuming the contact angle to be between 15° and 30° [6], it is possible to calculate the capillary pressure as a function of the capillary radius.

Table C-2.Capillary pressure values: estimated from experiments and theoretical.

	Heartwood	***Sapwood***	***φ = 15 °***		***φ = 30 °***	
			r =10 µm	***r =15 µm***	***r =10 µm***	***r =15 µm***
P_c (experiments), atm	0.07	0.07	-	-	-	-
P_c (from *Eq.C1*), atm	3.93	1.49	-	-	-	-
P_c (Jurin's law), atm	-	-	0.14	0.09	0.13	0.08

As can be seen from Table C-2, the values of capillary pressure calculated based on Jurin's Law are in the same range as those estimated from the experiments. The differences in values may be due to variations in the contact angles within the wood capillaries and their radiuses. Based on this, it can be suggested that Jurin's Law (*Eq.C2*) can reasonably describe the influence of capillary pressure on the liquid penetration process.

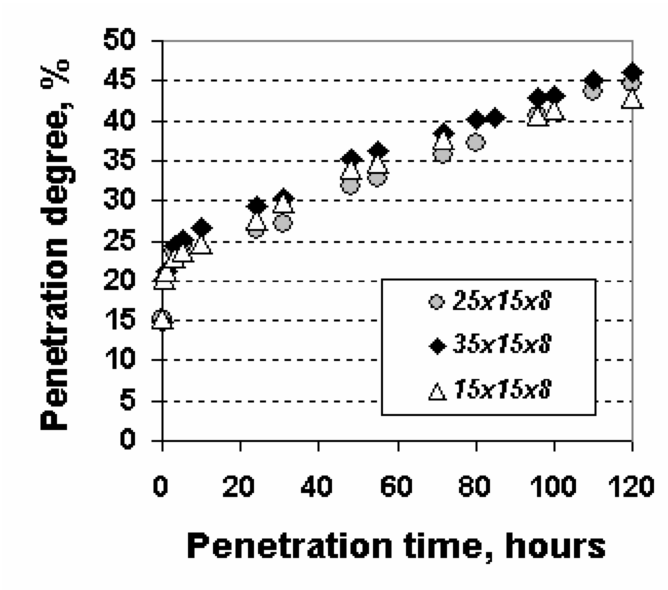

Figure C-2. Penetration of cold water into pine heartwood chips with different length.
Legend describes the chip dimensions in mm: length, width, and thickness.
Penetration conditions: no over-pressure, temperature 20 ºC.

Figure C-2 shows the long-term penetration of water into pine heartwood chips with three different length dimensions. As can be seen, the efficiency of penetration is practically the same for chips with different lengths. After fast initial uptake, water gradually penetrates into the chips. The increase in penetration degree is almost linearly dependent on the penetration time. This long-term water penetration was continuously accompanied by the release of air bubbles from the chips. It seems that penetration takes place mainly because of the gradual escape of entrapped air from the chips. The following mechanism can be suggested: The pressure of the compressed air is slightly over atmospheric pressure, so dissolution of entrapped air into penetrating water is expected. The dissolved air then diffuses towards the chip surface. Since the bulk water outside of the wood chips is under atmospheric pressure, part of the dissolved air will turn into gaseous phase. This is why the release of air bubbles was observed during the experiments. Air dissolution and diffusion at low temperature (20 °C) are quite slow processes. As a result, penetration of water with no over-pressure is also a very slow process (Figure C-2).

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