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# **IMPREGNATION, VAPOR PHASE AND METHANOL AS MEANS OF INTENSIFYING THE SOFTWOOD KRAFT PULPING PROCESS**

Eric Enqvist

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 the Auditorium of Puu2 at Helsinki University of Technology (Espoo, Finland) on the 27<sup>th</sup> of October, 2006, at 12 noon.

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Department of Forest Products Technology  
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<b>HELSINKI UNIVERSITY OF TECHNOLOGY</b> P. O. BOX 1000, FI-02015 TKK <a href="http://www.tkk.fi">http://www.tkk.fi</a>		<b>ABSTRACT OF DOCTORAL DISSERTATION</b>	
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Opponent(s)	Dr. Bruce Fleming, Professor Richard R. Gustafson		
Supervisor (Instructor)	Professor Panu Tikka		
<b>Abstract</b> <p>The objective of the research was to find ways to shorten the cooking time, i.e. intensify the kraft pulping process. The reason for undertaking such a study lies in the long standing trend of ever increasing reactor size in the kraft pulping industry. The huge digester size in use presently has lead to severe problems in understanding the behavior of the chip column inside the digester. An intensified process with a drastically shorter pulping time would give a more manageable process and greater freedom in reactor design.</p> <p>The study was performed using a new experimental digester giving a much greater control over temperatures than what can be achieved with other types of digesters. This enabled experiments that clarify the impact of impregnation, heat-up time, cooking temperature and cooking time to a greater degree than what has been possible earlier. The research on actual intensification centered on understanding the impact of impregnation and the impact of alcohols (methanol) on the overall rate of pulping.</p> <p>This research supports earlier research that shows how the cooking time can be shortened using alcohols as additives in pulping. It also supports results showing that a fast process can be achieved by using impregnation with high concentrations of cooking chemicals followed by a cooking stage performed with direct steam heating. The fact that the effects work in synergy so that the fastest pulping process identified was one that employed high concentration impregnation followed by heating using methanol steam is a new finding. The decrease in cooking time compared to a conventional liquid phase batch process without proper impregnation is close to 70%.</p> <p>The present research was aimed only at shortening the cooking time and does not address questions related to actual digester and process design and economical feasibility of the process. Especially the regeneration of cooking chemicals and methanol are an area that will need further study before such question can be addressed.</p>			
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Övervakare Professor Panu Tikka			
(Handledare)			
<p>Sammanfattning (Abstrakt)</p> <p>Undersökningens mål var att finna metoder för att förkorta koktiden, m.a.o. intensifiera sulfatkoket. Bakgrunden till undersökningen står att finna i den långvariga trenden mot allt större kokare i cellulosaindustrin. De enorma kokarna som används idag har lett till stora problem i förmågan att förstå vad som egentligen sker i flisbädden inuti kokaren. En intensifierad process med dramatiskt kortare koktider skulle vara lättare att styra och samtidigt ge mera frihet i processdesign.</p> <p>Studien utfördes med hjälp av en ny typ av experimentell kokare, som gav betydligt större kontroll över koktemperaturen än vad som varit möjligt med tidigare kokare. Detta gjorde det möjligt att utföra experiment som klargjorde inverkan av impregnering, uppvärmningstid, koktemperatur och koktid i en högre grad än tidigare. Forskningen gällande egentlig intensifiering koncentrerade sig på att förstå inverkan av impregnering och alkohol (metanol) på den totala koktiden.</p> <p>Forskningen stöder tidigare resultat vilka pekar på att koktiden kan förkortas genom att tillsätta alkohol i sulfatkoket. Forskningen stöder även resultat vilka visar att koket kan utföras mycket snabbt om veden först impregneras med höga koncentrationer av kokkemikalier och sedan upphetas med ånga i ett kort koksteg. Ett nytt rön är att dessa effekter kan utnyttjas synergistiskt. Den snabbaste möjliga kokprocessen som identifierades var en som använde impregnering vid hög koncentration följt av upphettning med hjälp av metanolånga. Förkortningen av koktiden jämfört med ett konventionellt vätskefaskok utan ordentlig impregnering är nära 70%.</p> <p>Denna studie ämnade endast förkorta koktiden i sulfatkoket av barrved, och avser inte svara på frågor som gäller egentlig kokar- och processdesign eller den ekonomiska bärkraftigheten av denna typ av processer. Framförallt frågor kring återvinningen av kok-kemikalier och metanol är områden som måste studeras närmare innan frågor av detta slag kan besvaras.</p>			
Ämnesord (Nyckelord)		Sulfatkok, Organosolv, Alkohol, Metanol, Barrträd, Ångfas, Snabb delignifiering	
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For the practical laboratory work I would like to thank all the staff at SciTech Process Research and Nab Labs Prosessianalytiikka Oy in Rauma. I would especially like to thank Henri Pihala for all the cooking experiments and Jukka Kahelin, Olli Timonen and Jussi Piira for overseeing the practical side of the experiments and their thoughts and comments during the process.

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Otaniemi September, 2006

## Authors Contribution

The work in this thesis is based on co-operation between the Laboratory of Pulping and Environmental Technology of the Helsinki University of Technology and Metso Paper Pori Oy. The laboratory work was mainly performed at Lännen Laboratoriot (later SciTech Process Research) in Rauma. The work was supervised by Professor Panu Tikka and coordinated by a steering group consisting of Professor Tikka, Dr Heinrich Leopold, MSc Matti Luhtanen, one representative from the laboratory in Rauma and the author. The main contributions of the thesis are:

- Confirmation of previous researchers' findings on the importance of impregnation
- Confirmation of previous researchers' results on water steam-phase pulping
- Confirmation and further clarification of the effect of alcohols in kraft pulping
- Proof that alcohols need not be present in large amounts, enabling the use of alcohol vapor as a heating medium
- A new process concept by deploying alcohol as a vapor phase in kraft pulping
- Information on the effect of impregnation on the delignification rate

The author planned the experiments and was active in the development of pulping procedures at the laboratory in Rauma. As the pulping experiments were performed with a new type of digester, a great deal of work went into designing reliable experimental protocols.

The author compiled the results for review by the steering group and made recommendations for future research directions. After the decision on future research programs by the steering group, the author planned the practical testing parameters together with the representative of the laboratory and oversaw the completion of the research program.

The compilation and analysis of the results for the thesis was performed by the author. The author also planned and wrote both the literature review and the actual thesis.

## Symbols and abbreviations

AA	Active alkali	FKA	Fiber Kappa Analysis
AHQ	Anthrahydroquinone	FL	Free liquor
ASAM	Alkali sulfite anthraquinone methanol pulping	FT-IR	Fourier Transform Infrared
AQ	Anthraquinone	L:W	Liquor to wood ratio
C <sub>E</sub>	Concentration in entrapped liquor	MeOH	Methanol
C <sub>FL</sub>	Concentration in free liquor	m <sub>w</sub>	weight of wood sample
C <sub>impr</sub>	Concentration of impregnation liquor	o.d.	Oven dry
Cl nr.	Chlorine number	PI	Process intensification
Cold pH	pH measured at room temperature	PuPu	Push-Pull
DP	Degree of polymerization	T	Temperature
DMC	Dry matter content	ΔT	Temperature difference
DWC	Dissolved wood components	R	Gas constant
E <sub>a</sub>	Activation energy	WLI	White Liquor Impregnation pulping method
EA	Effective alkali as NaOH	Wt%	weight percentage
EL	Entrapped liquor	VP	vapor phase
EtOH	Ethanol	WL	White liquor
		κ-nr.	Kappa number
		ρ <sub>w</sub>	basic density of wood
		ρ <sub>w.solid</sub>	density of wood cell wall

## Terminology

Alkali charge	Total amount of alkali added to the process
Alkali to cook	Amount of alkali actually entering the cooking stage
Alkali uptake	Alkali transferred to wood in impregnation
Cellulose	Primary component of the cell wall in wood
Chemical pulp	Wood defibrated using chemicals that dissolve lignin
Entrapped liquor	Liquor inside wood after impregnation
Hemicellulose	Heteropolymer present in cell wall along with cellulose and lignin
H-factor	Variable capturing both time and temperature in pulping
Kraft pulping process	Chemical pulping using sodium hydroxide and sodium sulfide
Lignin	Organic polymer that holds the cells (fibers) together in wood
Lignin yield	Percentage of original lignin left after pulping
Mechanical pulp	Wood defibrated using mechanical energy
Mercaptans	Organic compounds containing a functional group composed of sulfur and hydrogen, the compound giving the kraft process its distinctive smell
Penetrated liquor	Liquor that has entered wood through penetration
Rejects	Fiber bundles insufficiently delignified in the cook to yield free fibers
Screened yield	Total yield less screening rejects
Total yield	The amount of solid material left after cooking
Soda pulping	Alkaline pulping without sulfur
Total yield	Weight of pulp after pulping
Organosolv	Pulping using organic solvents
Wood alkali consumption	Actual amount of alkali consumed in reactions during impregnation



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**Appendixes**

1. Calculations of Heat Transfer and Temperature Profiles in Oil Bath Autoclave Digesters
2. Data tables, tests grouped according to experimental section in which the experiments are presented

# 1 Introduction

## 1.1 Background and research problem

With the exception of agriculture and fishing, the wood products industry is a unique industry in that it uses a completely renewable raw material and, in chemical pulping, produces a surplus of energy. Wood is also an exceptionally abundant raw material. The total production of roundwood (including wood for fuel) in the world in 2003 was 3.3 billion m<sup>3</sup>, about half of which was used for industrial purposes. This corresponds to roughly 1.3 billion metric tons of wood. Consequently, the amount of wood used in the world is of the same order of magnitude as the total production of cereals, which amounted to 2.0 billion metric tons in 2003/1/.

With rising energy prices and growing environmental concerns it is becoming increasingly important to use the wood raw material as efficiently as possible. The need for efficiency also applies to the production of papermaking pulp. The dominating process for turning wood into chemical pulp for papermaking is the kraft pulping process. Of the 131 million tons of chemical pulp produced in 2000 kraft pulping accounted for 117 million tons /2/. Kraft pulping is characterized by the use of aqueous solutions of alkaline chemicals (NaOH and Na<sub>2</sub>S) together with high temperature (140-180°C) to dissolve the lignin in the middle lamella that holds the fibers together in wood.

Kraft pulping has become the dominant way to produce chemical pulp because it yields strong pulp, can be used to process any fibrous raw material and generates an energy surplus. Kraft pulping is a complex system of simultaneous mass transfer and reactions /3/. The high temperatures, pressures and highly alkaline conditions used in kraft pulping make it very hard to accurately measure the different parameters affecting cooking, both in industrial equipment and on laboratory scale. This has led to a situation where the process design relies heavily on experience, and design changes are made in small steps rather than as step changes based on solid science. This reliance on small incremental changes has in turn has led to a situation where the digesters have become extremely large and hard to control. As a result of this trend, the capital cost of new digesters has risen and the flexibility of the industry has been severely restricted. The realization that this is a problem is not new; in 1930 Aronovsky and Gortner concluded that: “the cooking process in the pulp industry is based more upon practical experience than upon the knowledge of the chemical reactions taking place in the digester”/4/.

The reason why wood pulping is so notoriously hard to describe accurately is largely due to the complex nature of the raw material. Wood comes to the pulp mill in the form of logs with all the variation a natural raw-material brings with it. To make it possible to process the wood chemically it has to be turned into chips. In order to avoid excessive cutting of fibers, the chips can not be too small. A typical wood chip in pulping is around 25 mm long, 15 mm wide and 5 mm thick. As a typical softwood fiber is just over 3 mm long and 30 µm thick, a single chip may contain more than 0.5 million fibers /5/. This constitutes a natural source of variation in wood density and moisture content, which is further increased by the tendency of wood to form early- and latewood with very different characteristics. Also, because of the nature of the transport phenomenon involved, it is impossible to avoid further unevenness when the wood gets into contact with the pulping

chemicals. On top of this, even on the level of individual fibers, there is huge heterogeneity in chemical composition and physical characteristics due to the layered structure of the wood fiber wall. The possibilities of influencing this problem are limited. In most chemical processes the raw material can be crushed to minimize the variations in the raw material. For wood, where fiber quality is critical for paper properties, this of course is not an option.

## **1.2 Concept of process intensification**

With increasing understanding of reaction kinetics and better process control equipment, many industrial chemical engineering processes have become more compact and thus more efficient. When reactors are made smaller, in-process inventory is reduced and thus the risk of continuous production of sub-standard products is also significantly decreased. The discipline in chemical engineering aimed at decreasing reactor size and maximizing the efficiency of industrial processes is often referred to as process intensification (PI). PI is not a method as such, but rather a framework for various methods striving to achieve more intelligent processes.

Several slightly different definitions of PI exist. Some define it as the reduction in size of process equipment by a factor of 100, others are less ambitious, setting the aim at halving the reactor volume for a given rate of production [6,7]. This thesis does not try to define the concept of PI in any definite way, but is more concerned with viewing kraft pulping through the lenses of the basic process intensification mentality. The basic goal of process intensification is to measure the true kinetics of the chemical reactions and make sure that mass- and heat transfer correspond to those kinetics. The idea is to ensure that the streams of the purest reagents possible meet and are supplied with adequate energy to react at the point of contact. Ideally, in an intensified process, all molecules in the whole system get the same treatment. This requires that the mass transfer and kinetics of the process are designed so that the reaction kinetics is the limiting factor of the process. The leading thought in intensified processes is to avoid large reactors with back-mixing and slow addition of chemicals that slowly diffuse and react with some other reagent. Process intensification has its background in attempts to reduce the capital cost of production systems in the chemical industry. PI has been successfully applied in some chemical engineering applications, such as de-aeration of water and combined distillation and reaction in esterification. Static mixers in pipelines are another example of PI [8]. However, there has not yet been a major commercial breakthrough of the concept in wider process design, with the exception of some special applications. This has been due both to technical and economical reasons but also aversion of risk in the relatively conservative chemical industry.

### **1.2.1 Current situation in kraft pulping process design**

Contemporary kraft pulping processes are in strong contrast to any concept of intensification. Despite research on kinetics, residence times in reactors have only become longer over the years. This is due to decreased cooking temperatures and chemical concentrations in pursuit of greater heat efficiency and so-called modified pulping aimed at reaching lower pulp lignin contents prior to bleaching. Also, increased production capacities have led to bigger reactors and the reactors are now reaching sizes where the chip column non-uniformity is starting to present a serious obstacle to the production of uniform-quality kraft pulp. For instance, large temperature differences (5°C

in the cooking zone, up to 70°C in the displacement zone) and flow speed differences have been measured for liquid removal screens on different sides of a modern continuous digester /9/. The striking thing about the evolution of kraft pulping systems is that there has never been a conscious decision to steer the development onto a path of ever-increasing reactor size and residence times – it has all just happened. All changes in process technology have been gradual and based on an earlier small step, eventually leading to the huge digesters of today. Nobody has made an effort, since the late 1960's, to systematically study the kraft process from a point of view that would resemble intensification. Some more recent studies have been performed aimed at removing the problems related to sulfur, but in these cases the aim has been to keep the overall process efficiency at the same level as in kraft pulping, not to improve on it.

It can be envisioned that by gaining a better understanding of what the actual limiting factors are for kraft pulping, processes could be designed to operate at their maximum efficiency. If current processes do not operate at this “efficiency barrier”, it is clear that a move towards that barrier would make it possible to reduce the digester volume for a given production rate. Again, the idea is not new: in 1964 Theodore N. Kleinert wrote: “It was felt that mere variation of factors in pulping under conventional conditions as practiced in the industry cannot lead to major improvements in the technology of pulping and that better knowledge of the underlying basic phenomena could lead to new commercial processes”/10/.

### **1.2.2 Process intensification in kraft pulping**

In order for any chemical reaction to take place, reactive chemicals and energy have to be present. The rate of reactions as a function of chemical concentration and temperature is given by the reaction kinetics. In chemical pulping the reactions take place inside the wood matrix, meaning that the kinetics are dependent on the heat- and mass transfer into the wood.

In pulping systems, heat transfer is achieved either by putting the wood in contact with a hot liquid or by letting steam condense on the wood surface. Heat transfer in wood is at least one order of magnitude faster than mass transfer. Therefore, it is clear that heat transfer is not a limiting factor for process speed /11/. The actual absolute temperature used industrially is then a question of optimizing the steam usage of the mill. Medium-pressure steam from the steam turbines is generally used, which sets the maximum temperature at around 180°C. The steam pressure is generally 12 bar, corresponding to a temperature of 188°C.

Compared to heat transfer, the transfer of chemicals into the wood is much more complicated, especially in view of the alkali-consuming reactions taking place in wood and the vastly varying temperature dependence of their kinetics. The purpose of pulping is to break lignin bonds, dissolve the lignin into the cooking liquor and simultaneously remove part of the hemicelluloses. This can only take place in an alkaline environment with cold pH above 11 (pH measured for samples cooled to room temperature). The real difficulty in ensuring such conditions becomes apparent by looking at the various alkaline-consuming reactions when increasing the temperature to the level needed for delignification, i.e. above 140 °C. The actual lignin bond cleavage does not consume very much alkali, as seen in Table 1.

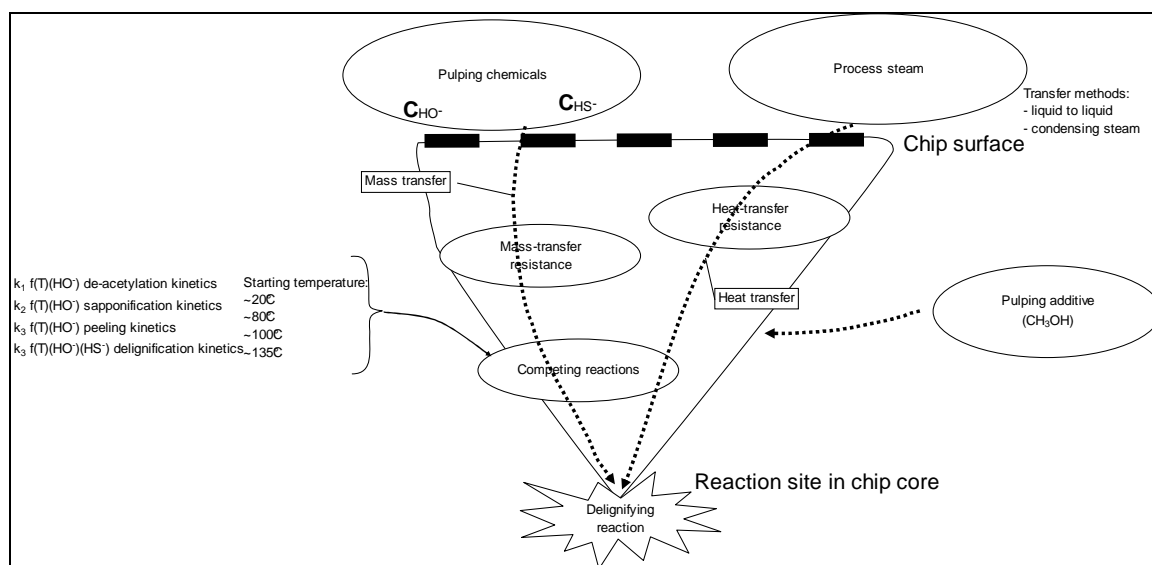
**Table 1. Consumption of alkali in the basic reactions of softwood pulping. Alkali consumption is 150 kg EA/t wood as NaOH for a final pulp lignin content of 3%. Total pulp yield 47% /5, 12/.**

Reaction	Approximate temperature of significant reaction speed (°C)	Alkali consumption (kg NaOH/t wood)
Hydrolysis of acetyl groups	20	15
Hemicellulose degradation reactions	100	45
Neutralization of peeling products	130	50
Neutralization of dissolved lignin	140	40

By the time a temperature suitable for lignin cleavage is reached (~140°C), about half of the total alkali charge has been consumed. Maintaining favorable alkaline conditions for delignification in all parts of chip pieces is a real challenge and today's kraft cooking technology does not do this. Several studies and modeling work prove that alkali depletion in the chip interior is a fact and a major drawback in contemporary cooking technology /13/.

In aiming for process intensification and fast heating, the crucial issue is to have enough alkali in the molecular vicinity of the lignin-containing fiber wall structure. It is easy to hypothesize that this can only be achieved by impregnation, using highly concentrated cooking chemicals at low enough temperature. Finding the conditions to achieve this aim is one of the starting hypotheses of the present work.

Figure 1 is an attempt to schematically present the basic relationships governing the speed of delignification in kraft pulping. The figure illustrates how the mass transfer has to overcome both the mass transfer resistance and the consumption of chemicals caused by competing reactions. The speed of the competing reactions is dependent on absolute temperature. Heat transfer depends on the temperature difference and the heat transfer resistance of the wood. Certain pulping additives such as methanol have an impact on different aspects of the whole process leading to faster overall pulping.



**Figure 1. Schematic presentation of factors affecting delignification reactions.  $k_x f(T)(OH^-)$  symbolizes the different alkali consuming reactions as functions of temperature.**

### 1.3 Objectives

The objective of the investigation was to find ways to intensify kraft softwood pulping. In this investigation the term intensification was understood to mean a faster overall pulping rate, i.e. a reduction of the overall process time. This means smaller reactors and smaller in-process inventory. The benefits expected from an intensified process would be more flexible reactor design, less undesired side reactions and easier process control. Further possible benefits include lower consumption of pulping chemicals and higher pulp yield. A minimum requirement for an intensified pulping process was to increase process speed without impairing the raw material efficiency of the process, both in terms of pulp yield and chemical consumption.

### 1.4 Starting hypotheses

The process time can be reduced by increasing the efficiency of heat- or mass transfer or the rate of the reactions. The basic starting hypotheses were:

- (1) Heat transfer is a straightforward way towards process intensification; steam phase cooking is the fastest means of heat transfer known in industrial pulping.
- (2) Mass transfer of cooking chemicals is the limiting factor for pulping speed and the obstacle to taking advantage of fast heat transfer; an intensified kraft process must have a high concentration of cooking chemicals in the vicinity of wood lignin at the onset of reactions
- (3) Methanol increases pulping speed

Based on earlier experience, two approaches to intensifying the kraft softwood pulping process were seen as particularly promising at the onset of the project. These were optimizing the front end of kraft pulping, i.e. improving impregnation through the use of



high concentrations of pulping chemicals in chip impregnation, and using short-chained alcohols as pulping accelerants.

## **1.5 Research methods**

The research was mainly conducted through laboratory cooks and basic pulping-related analysis methods. A new type of experimental digester was used in the project in order to make it possible to vary the cooking parameters over a very broad range. Most of the research presented in this thesis was performed using this equipment. The idea of the present investigation was to use fundamental laboratory tests to chart the possibilities of achieving faster and more uniform delignification using different impregnation and heat-up scenarios and by using organic solvents in kraft pulping.

Some basic impregnation tests were also performed. These were done with the impregnation unit designed in the laboratory of pulping technology at the Helsinki University of Technology. The equipment can be used to measure how penetration advances under different conditions.

Some pulp uniformity tests were also performed using both fiber kappa analysis and Fourier Transform Infrared Spectroscopy (FT-IR) measurements. Both methods measure the uniformity of the lignin removal in cooking, fiber kappa analysis one fiber at a time and FT-IR measurements from the surface of a pulp pad.

All methods used are presented in greater detail in the experimental section of the thesis.

## **1.6 Scope of research**

In the current project, small-scale laboratory pulping tests were used to investigate the possibilities for intensifying the processes. The results of the trials were mainly evaluated based on the rate of delignification, process yield and process uniformity (rejects). The question of fiber quality was outside the scope of the research. Also, questions regarding actual plant design for intensified processes were left outside the scope as was a deeper analysis of the costs involved.

The methods of process intensification employed were chosen on the basis that they should be reasonably simple to implement on an industrial scale. Therefore, the additives used were cheap industrially available chemicals that are not exceptionally hazardous or poisonous in ppm concentrations. Also, any additives used should be easy to regenerate from the spent pulping liquor. As such, short-chained alcohols were known to hold great promise. The liquor to wood ratio (L:W) had to be technically reasonable and the end-of-cook alkalinity had to be reasonable in order to avoid a huge dead load to chemical recovery. Medium-pressure steam was considered as the heating medium. The reactor to be minimized was the actual digester. Processes taking place at atmospheric pressure were not considered essential to the overall process time, so impregnation was always performed <100°C as this can be performed at atmospheric pressure.

The study was highly experimental and evolutionary in nature. The aim at this point was to find possible ways of intensification. Where such possibilities were found, no attempt was made to optimize and completely explain the effects at this point. Instead, the idea

was to try to be technically innovative and to identify different scenarios that can be used in future research into more flexible processes.

## 2 Literature review

This literature review is aimed at identifying techniques previously studied for the intensification of kraft softwood pulping. There is a large body of literature available on different forms of process improvements for kraft pulping. This literature can be roughly grouped into the following categories:

- Descriptions of new digester designs, usually written by representatives of equipment manufacturers. Much of this literature describes the step change of mills going from old equipment run much over its designed capacity to modern equipment run at design capacity.
- Actual data on mill performance in daily operation. Very little material of this type exists.
- Research into modifications aimed at improving pulp viscosity and sometimes yield. This literature generally either serves as the basis for future digester design changes or is aimed at understanding the actual implications of the changes made. The question of overall process speed is rarely touched.
- Research into strength characteristics of pulp using different cooking and bleaching set-ups. Very little information on cooking efficiency can be derived from this literature.
- Reports on laboratory-scale processes using more or less realistic chemicals and conditions. A lot of pulping research has been performed without any consideration of the cost of possible additives etc.

In this review only research that is seen to decrease overall pulping time is considered as improvements towards intensification, so research aimed at increasing e.g. pulp yield or viscosity is not considered. Although the improvement of yield as such is not an aim, the overall efficiency of the process may not be sacrificed and in fact many process improvements actually bring with them increased yield. The question of pulp strength is not addressed except when the deterioration of strength is so substantial as to make the pulp unthinkable as a raw material for modern papermaking.

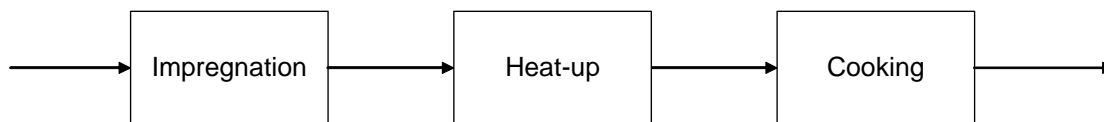
As presented in section 1.2.2 any decrease in the overall pulping time would have to come from faster heat-transfer, faster mass-transfer or faster reactions. In the following text different ways to improve all three are discussed after a short introduction to the basics of kraft pulping.

### 2.1 *Kraft pulping*

Kraft pulping is by far the most widely used way to produce chemical pulp today. The reasons why kraft pulping has become so popular include the versatility of the raw material base (all species of wood can be pulped), the low cost thanks to the use of pulping chemicals that are easy to regenerate, the energy surplus in the process and also the high fiber strength in the end product.

The basic idea in kraft pulping is to use alkali (NaOH) and sulfur ( $\text{Na}_2\text{S}$ ) at high temperature (140-180°C) to break down and dissolve the lignin that holds fibers together in wood. The wood is handled in the form of chips, with the chips submerged in an

aqueous solution containing the cooking chemicals. The process can be broadly divided into three steps, impregnation, heat-up and actual cooking, as seen in Figure 2. The aim of impregnation is to transfer cooking chemicals into the wood, with heat transfer taking place in the heat-up stage and the actual reactions in the cooking stage. In reality, these steps are not clearly separated and take place simultaneously.



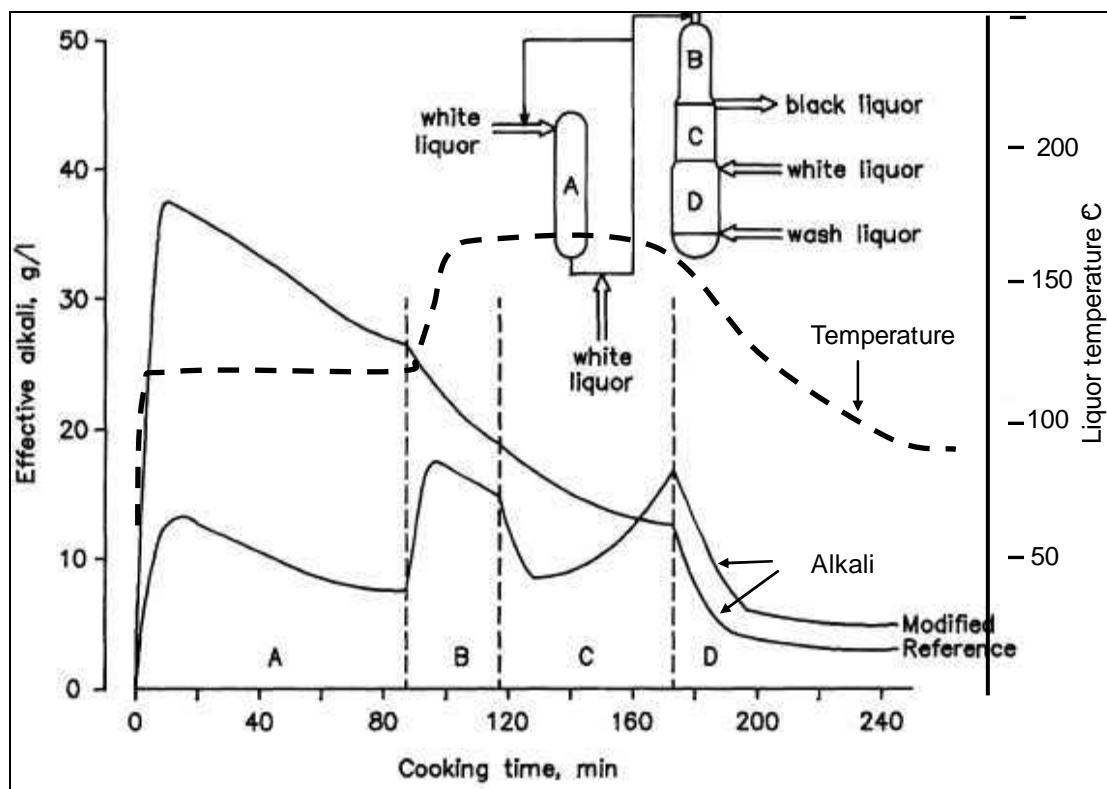
**Figure 2. Basic process steps in kraft cooking.**

The basic process steps taking place during the cooking stage are:

- transfer of chemicals to the liquid-wood interface
- transfer of chemicals inside the wood
- reactions between the chemicals and wood constituents
- removal of reaction products from the wood to the pulping liquor

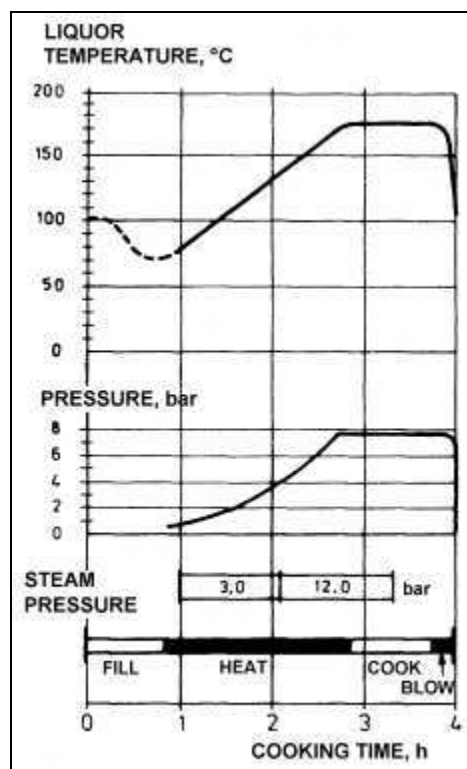
Kraft pulping is generally considered to be restricted by the speed of the reactions. In the following review, all steps will be discussed at some length to identify possible ways to increase pulping speed.

On an industrial scale, kraft pulping is performed either as a continuous process in very large vertical digesters or in displacement-heated batch digesters. In continuous pulping, the chips are fed at the top of the digester together with the pulping chemicals to form the chip bed inside the digester. The chip bed moves slowly downward inside the digester and after a retention time of around 4-6 hours the delignified chips exit through the digester bottom. Modern continuous digesters can be around 60 meters high and up to 10 meters in diameter. The temperature and active chemical profiles in a continuous cooking installation are shown in Figure 3.



**Figure 3. Concentration profile of effective alkali and temperature profile in modified and conventional continuous cooking; temperature curve added to original picture /5/.**

In industrial batch pulping a fiber line consists of several, typically 6-8, individual digesters that are used in a batchwise manner to ensure more or less continuous production. The cooking cycle of an individual batch digester is presented in Figure 4. As can be seen, the total process time is around 4 hours with both methods. In continuous pulping the impregnation stage (stage A in Figure 3) is preceded by chip steaming. This adds around 30 minutes to the process time.

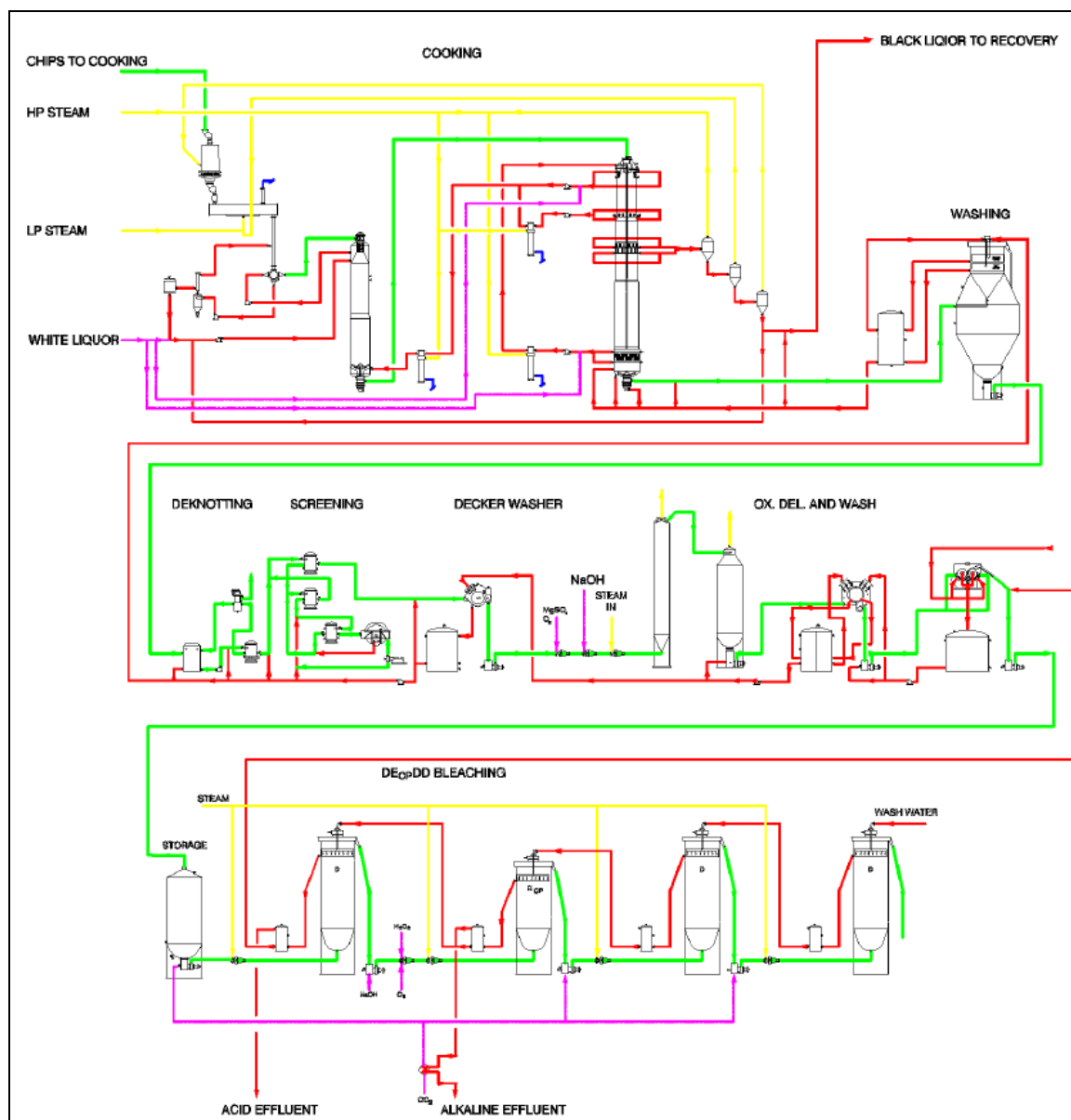


**Figure 4. An example of timing and process conditions in a conventional batch kraft cooking system [5].**

The main drawbacks of the kraft process are:

- capital-intensity; especially the regeneration of chemicals requires such complex equipment that mills have to be built for very big production rates in order to be profitable. This has led to huge investments and therefore increased the financial risks involved in building new pulp mills
- dark pulp; this leads to a need for multistage bleaching after the pulping stage, which increases the waste water loads and causes to further investment needs in water treatment equipment
- odor problems; the sulfur used in the process forms malodorous compounds that the human nose detects at very low concentrations. Also, there is a slight risk of smelt-water explosions in the chemicals recovery department. These two factors have been cited as reasons why not to build pulp mills close to densely populated areas.

After the actual cooking stage, the delignified chips are washed and delignified further using oxygen. The oxygen delignification is followed by multistage bleaching to remove the remaining lignin and ensure a sufficient final brightness. A typical modern fiber line using continuous cooking can be seen in Figure 5.



**Figure 5. Flowsheet of cooking, washing, screening, oxygen delignification and DE<sub>op</sub>DD bleaching [5].**

The balance of lignin removal can be different in different mills. At some mills as much of the lignin as possible is removed in cooking, whereas other mills leave a higher lignin content in the chips after cooking and instead remove more lignin in the yield-saving bleaching stages. Factors such as the cost of wood and bleaching chemicals and the chemical recovery capacity determine the optimal level at individual mills.

The extent of delignification achieved is generally measured by letting the pulp react with a known amount of some chemical for a given time. After the reaction time the residual chemical is measured, generally by titration. The most frequently used method is kappa number measurement, which is performed using potassium permanganate. Another method that used to be in widespread use is the chlorine number, using chlorine as the active chemical. The relationship between the methods and pulp lignin concentration is shown in Table 2.

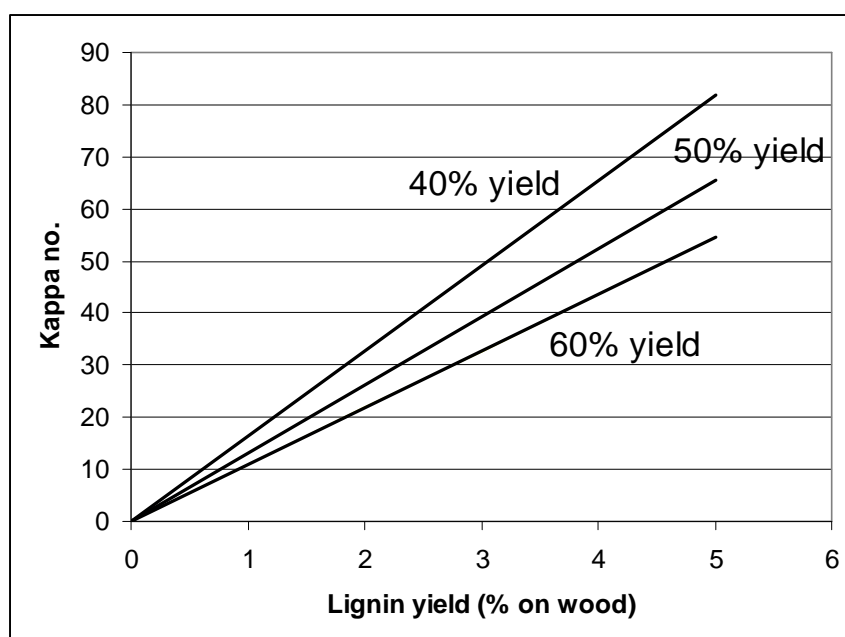
**Table 2 Examples of relationships between Kappa and chlorine numbers and residual lignin content in kraft pulping /5/.**

Wood species	Cl- number/L <sup>1)</sup>	κ- number/L <sup>1)</sup>
Birch	0.991	6.064
Pine, Spruce	1.109	6.546

<sup>1)</sup>Lignin content

There is one significant drawback with using kappa or chlorine numbers for determining the extent of delignification. The measurement gives only the ratio of lignin structures to the weight of the pulp sample. This means that the amount of lignin left in the pulp is not at all compared to the original lignin in the wood. In other words, although the delignification of the wood might have proceeded very differently in two cooks, the kappa number can be the same, provided that the carbohydrate yield has changed in the same way as the lignin removal.

A simple way to circumvent the problem is to use the total process yield and the relation presented in Table 2 to calculate the lignin yield on wood of the process. This can then be readily compared to the original lignin content of the wood. An example of the impact of varying process yields on the relationship between kappa number and lignin yield is illustrated in Figure 6.



**Figure 6. Kappa number as a function of lignin yield for pulp with a total yield of 40, 50 and 60% on wood.**

Normal softwood contains 26-32% lignin /65/. The industrially interesting lignin yield range after cooking is 1.5-2.5% lignin on wood, corresponding to a total yield of 45-50% on wood.

An often measured parameter for chemical pulp is pulp viscosity. The viscosity gives an idea of the degree of depolymerization of the cellulose molecules of the pulp. There are several other factors such as hemicellulose content that also affect viscosity. An excessive



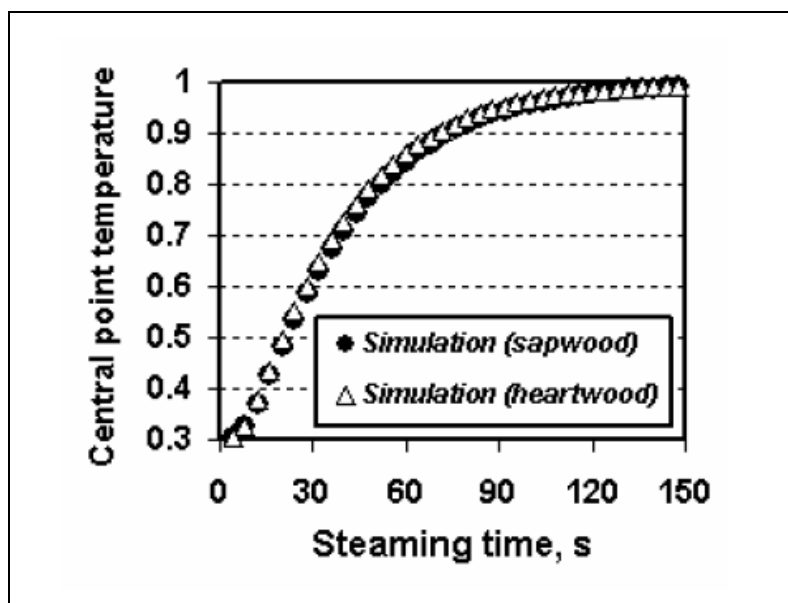
viscosity drop in bleaching is a sign of pulp degradation. As far as the viscosity of brownstock pulp is concerned, it is not a good measure of pulp quality /14/.

## **2.2 Intensification by improved heat transfer and higher temperature**

One of the basic factors determining process speed is the availability of heat for the reactions. The general theme of heat in pulping can be divided into two basic questions, the question of heat transfer and the question of absolute temperature in pulping. The following is a discussion of their effects on overall process speed.

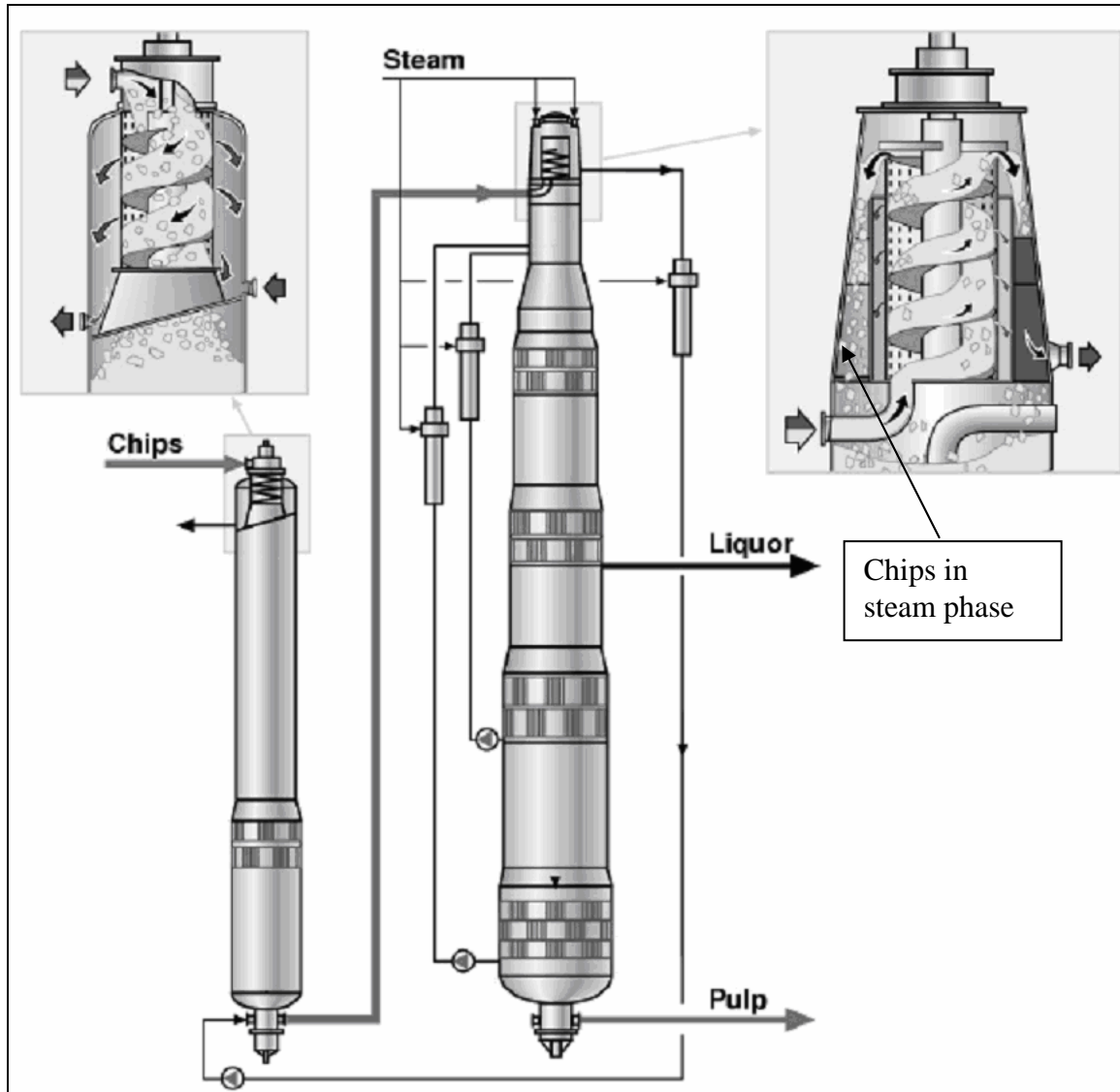
### **2.2.1 Heat transfer**

On an industrial scale, heat transfer to wood is possible in two ways, either by condensation of steam on the wood surface or by contact with a heating liquor. In both cases the transfer of heat is dependent on the temperature difference between the heating medium and the wood. As a general principle, it can be assumed that the diffusion coefficient for heat transfer in wood is up to two orders of magnitude larger than that of mass transfer /11/. In other words, it is at least 100 times easier to transport heat than mass in wood. This means that, if they occur simultaneously, mass transfer will be the rate-determining step.



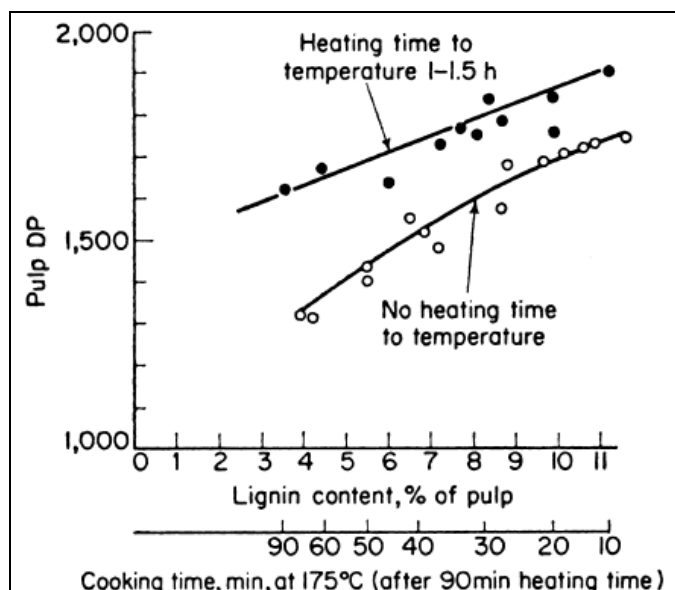
**Figure 7. Heating of pine chips by saturated steam of 100 °C Starting temperature: 30 °C; Chip dimensions: 25x15x8 mm /22/.**

As can be seen in Figure 7, heating with condensing steam is very rapid. The same principle is applied in some modern continuous digesters to reach the desired pulping temperature by having a portion of the top of the digester in steam phase as shown in figure 8.



**Figure 8. A two-vessel steam/liquor digester system (Kvaerner) /5/.**

From a pulp quality point of view, however, it is generally agreed that heating to cooking temperature should be slow, as fast heating is said to be detrimental to pulp quality. This is an interesting claim as the heating of chips in steam is quite rapid, as seen in Figure 7, and also the heating to cooking temperature after impregnation is fast in modern displacement heated batch and continuous digesters. The claim that pulp quality suffers from fast heating up is based on rather old research, such as the findings regarding the relationship between heat-up time and pulp polymerization degree measured as pulp viscosity, as presented in Figure 9.

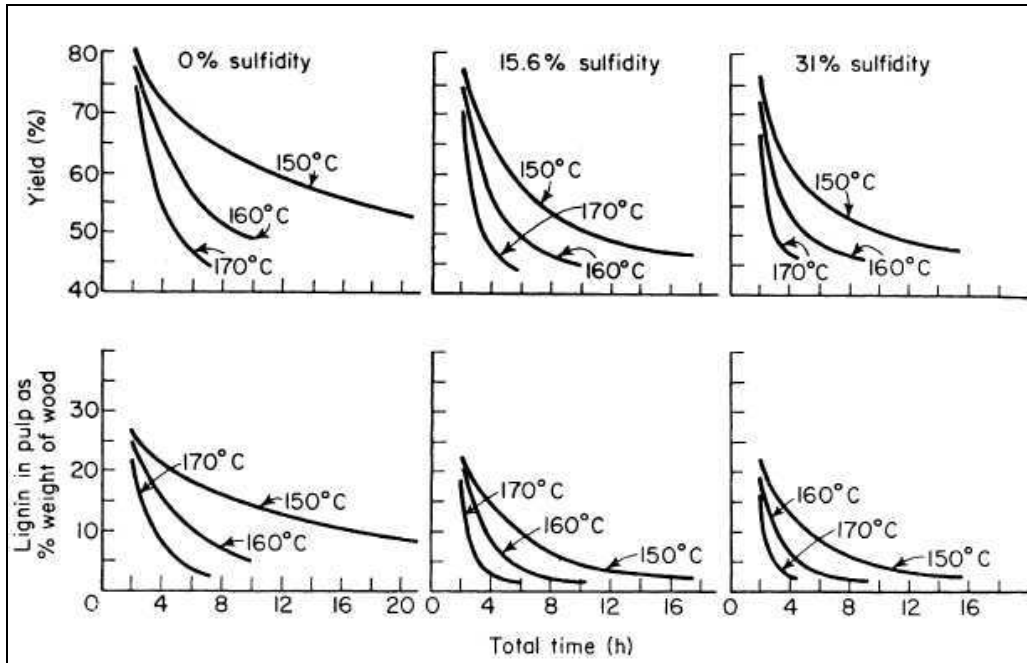


**Figure 9. Degree of polymerization vs. lignin content in kraft pulping of slash pine, with slow or instantaneous heating to cooking temperature /20/.**

A difficulty in examining the effect of the heat-up time is that it is very hard to accurately conduct tests over a wide range in the laboratory. Current pulping research techniques do not allow pulping tests with different types of impregnation and a very short heat-up time. For instance the results in Figure 9 are based on cooks without proper impregnation. Instead the wood was merely pre-evacuated at relatively low temperature and then brought into contact with hot cooking liquor.

### 2.2.2 Absolute temperature in pulping

It is well known that the pulping temperature has a very significant impact on the overall pulping speed. In its most basic form the temperature dependence of basic kraft cooking can be seen in Figure 10. The figure also shows the impact of sulfidity, which will be discussed later; normal industrial cooks have a sulfidity of 30-40%.



**Figure 10. Effect of cooking time, temperature and sulfidity on the rate of kraft cooking of spruce. Heating time 2 h, active alkali charge 242 kg/t wood as NaOH /12/.**

The relationship between cooking temperature and delignification can be modeled using an Arrhenius-type activation energy model, the so called H-factor model. The basic form of the Arrhenius equation for the temperature dependence of the rate constant  $k$  is seen below.

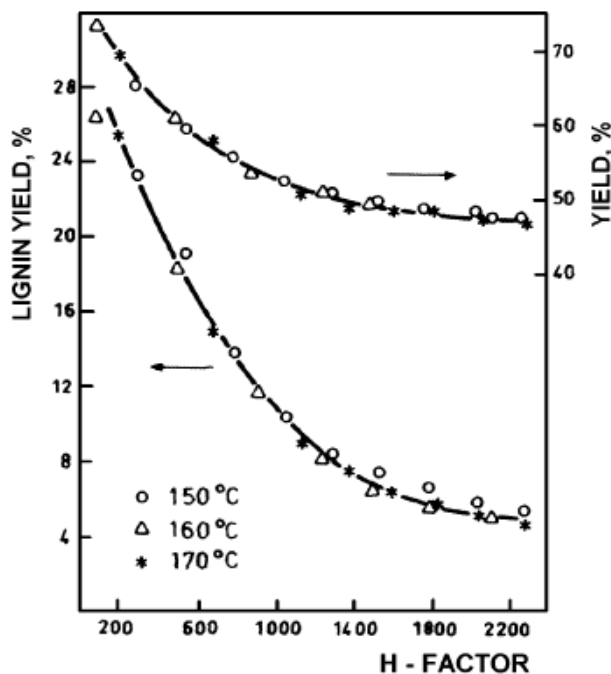
$$k = Ae^{-\frac{E_a}{RT}} \quad \text{Equation 1}$$

where  $E_a$  is the activation energy for the reaction  
 $T$  is the absolute temperature  
 $R$  is the general gas constant

This rate equation holds for the average degree of delignification observed in the process when the starting parameters are held constant. By experimentally determining a value for the activation energy and setting a reference value of reaction speed at 100°C it has been possible to construct a method of calculating the combined effect of time and temperature as an expression called the H-factor. The H-factor model does not take into account the effect of chemical concentration, but it is a good tool when comparing cooks with different temperature profiles. The essential rule of thumb that can be derived from the H-factor is that the rate of reaction roughly doubles with every 10°C increase in temperature.

The effect of describing the cooking time and temperature with the help of the H-factor can be seen in Figure 11. Comparing this against Figure 10, the usefulness of the H-factor becomes apparent. It is also clear that the cooking temperature does not have an impact on the cooking yield, or the ratio of lignin to carbohydrates in the pulp produced. This is supported by research by Daleski who used temperatures up to 195°C /15/. High temperature was, however, seen to have an effect on pulp viscosity. A similar study

conducted at HUT that included trials at both laboratory and mill scale also showed that viscosity goes down and rejects up when the cooking temperature is increased. No effect on total yield was seen. So, non-uniformity increases due to limits in mass-transfer, but yield as such is not affected /16/.

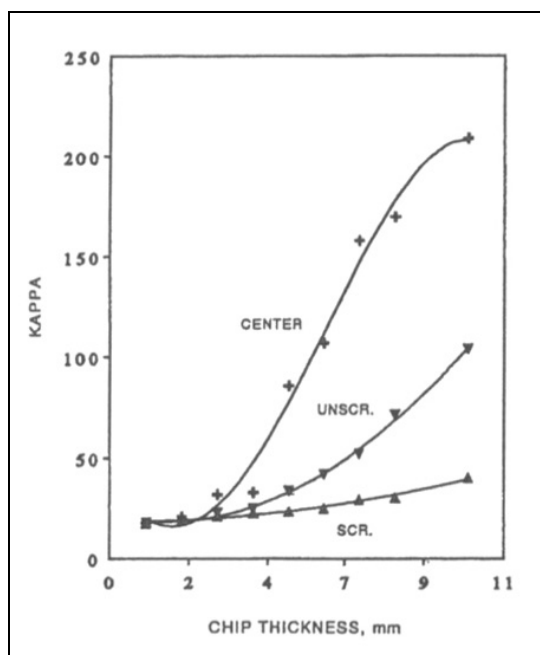


**Figure 11. Yield of pulp and residual lignin content in kraft cooking of spruce wood as a function of H-factor. Sulfidity 31% /5/.**

The basic H-factor model has been refined over the years. The most popular way to model kraft pulping is by dividing the cook into three phases, the initial, bulk and the residual phase. Time/temperature correlations are given for each phase separately as a function of liquor alkalinity. The effect of increasing the temperature is still the same, a faster cook. However, fast cooks have not been a priority in process development lately. This is probably largely due to energy economy. It has also been stated that the activation energy of delignification is lower than that of carbohydrate cleavage. This means that delignification is less temperature sensitive than the cleavage of carbohydrates. A reduction in pulping temperature should thus lead to more selective delignification, as lignin cleavage stays more or less the same, while carbohydrate cleavage is reduced /17/.

As discussed above, increasing the temperature is restricted by the need for uniformity in pulping. Laboratory trials have shown that thick chips are always unevenly delignified, so that 10 mm thick chips can have a screened kappa number (=average kappa number) of 24 and the chip center can still be at a kappa number of 127 /13/. The effect is accentuated with increased temperature. This phenomenon is illustrated in Figure 12. The nonuniformity leads to overcooking of the chip surface and a loss of yield and pulp strength. In fact, it has been shown that thin chips can be pulped to very low lignin content without loss of yield, indicating that the apparent unselectivity of kraft pulping is in fact unselectivity of the processing method and not the delignification chemistry. All this seems to imply that the transfer of chemicals really is a bottleneck in kraft pulping and that an improvement in diffusion based mass-transfer in impregnation would be a possible way to intensify the kraft process. The fact that non-uniformity in delignification

is due to uneven transfer of chemicals is further backed by research showing that the lignin content of the rejects is basically unchanged in cooks where the actual rejects content on wood has changed from 2 to 12% on wood /18/. The fact that the rejects always contain the same amount of lignin means that the rejects is due to lack of chemicals and therefore reactions in the chip center. The modeling by Gustafson et al. /19/ also shows that the reject content in pulp is dependent on the delignification profile rather than the absolute lignin concentration.



**Figure 12. Screened, unscreened and chip center kappa numbers of pulps from stratified laboratory cooks using 1-10 mm laboratory-cut chips. Bulk average kappa number 23.4 /13/.**

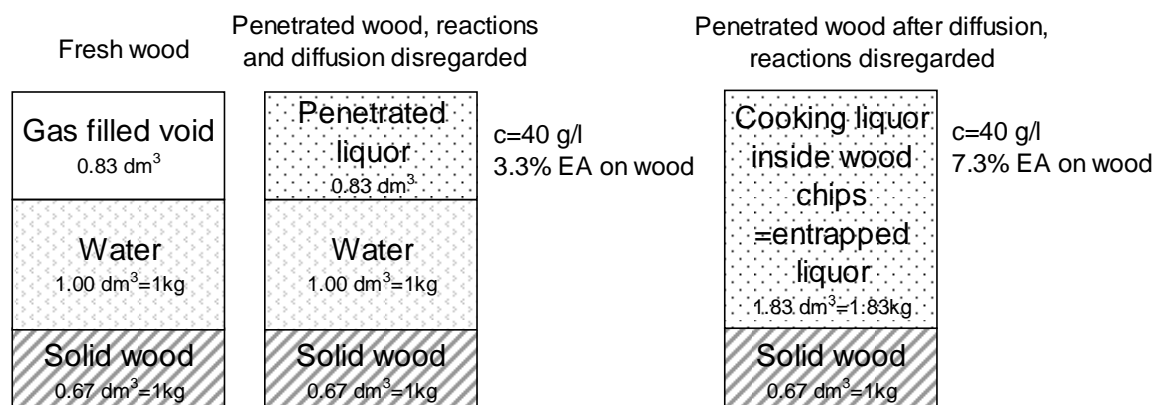
Consequently, from the point of view of intensification, the upper temperature limit is set by energy consumption considerations and the formation of rejects when pulping thicker chips at higher temperature.

### **2.3 Intensification by improved mass transfer**

If kraft pulping is constrained by mass transfer, an intensified process should be achieved by making sure the pulping chemicals are at the reaction sites in sufficient quantities when the reaction temperature is reached. Mass transfer of pulping chemicals into the wood takes places through two basic mechanisms: I. penetration and II. diffusion. Penetration refers to the process where the air in the wood chips is replaced by cooking liquor and diffusion is the random movement of molecules leading to the removal of concentration gradients. The behavior of these two methods of mass transfer has been studied extensively in the past and some interesting findings have been made.

The quantity of chemicals that can be transferred using the two mechanisms depends on the density, the dry matter content of the wood and the concentration of the impregnating liquor. Figure 13 shows an example of the volume fractions of a 1 kg block of fresh wood with a basic density of 400 g/dm<sup>3</sup> and a dry matter content of 50% being impregnated

with a 40 g/l EA liquor. Penetration will only fill the void space available, so any further mass transfer needed will have to rely on diffusion.



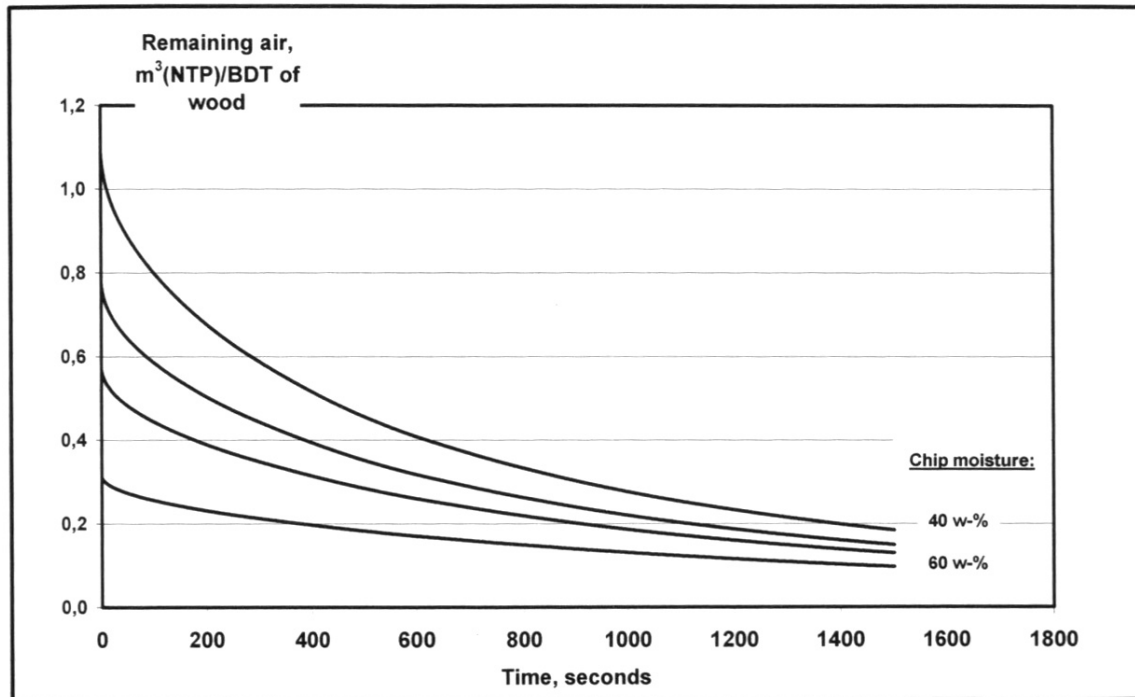
**Figure 13. Volumetric proportions of gas, water and solid wood in a hypothetical solid wood block of 1 kg dry matter with a basic density of 400 g/dm<sup>3</sup> and a dry matter content of 50% being impregnated with 40 g/l liquor. The wood represents a typical boreal softwood. The achieved alkali charge transfer to the wood as % EA on wood is indicated for the two cases.**

The total chemical consumption in softwood pulping is typically around 15% EA on wood weight as NaOH. In a hypothetical situation using the wood model above, where a 40 g/l EA cooking liquor is used, the chemical charge transferred by penetration would thus be only 3.3% on wood. If alkali consumption is disregarded and the volume of impregnating liquor is considered infinite (no concentration drop in the impregnating liquor), the charge transferred after complete impregnation and diffusion would be 7.3% on wood. A similar calculation can be found in the text by Nolan /20/. The result of the calculation implies that around half of the chemicals needed for delignification have to be transferred to the wood after the onset of the reactions, either during heat-up or during the actual cooking stage. The cooking stage is also where the bulk of the reactions take place.

### 2.3.1 Intensification through improved penetration

Fresh wood contains gas filled voids evenly spread out in the wood matrix. The filling of these voids with cooking liquor is referred to as penetration. There are two basic ways to improve penetration in impregnation, either by more efficient air removal or by applying higher pressure in impregnation. The basic principles have been known for a long time and have been presented as process ideas, such as the Va-Purge process etc., as far back as the 1950's. The basic idea of the Va-purge was to alternatively increase digester pressure using steam and relieving the digester for a couple of cycles in order to remove air entrapped in the chips. The benefits reported were lower rejects, shorter cooking times, higher yields and lower alkali consumption /21/. However, it was not until the work by Malkov /22/ that an accurate mathematical model describing the effect of the various parameters affecting penetration was presented. The research showed that the most important parameters in penetration are temperature, impregnation pressure, liquor viscosity and liquor surface tension. The modeling was further refined by Kovasin et al. /23/ who were able to calculate the time needed for the longitudinal diffusion of air out from softwood chips at different chip lengths and initial moisture contents. The diffusion

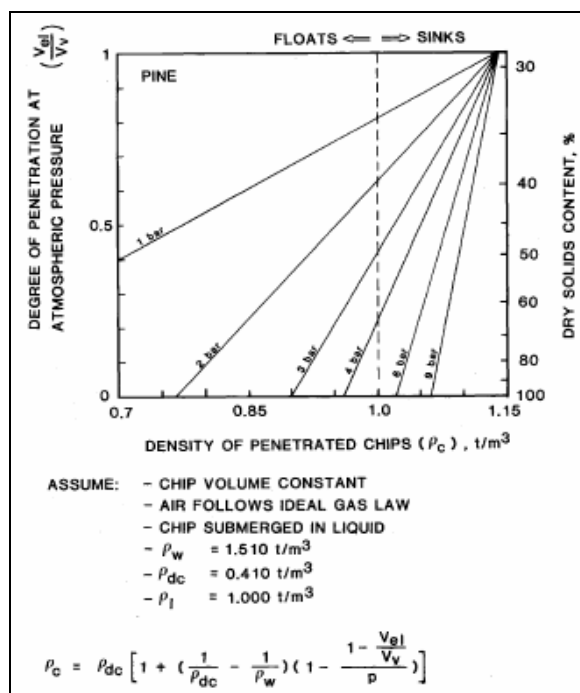
of air from the chips is a pre-requisite for complete impregnation. Figure 14 shows how air is removed from chips with varying dry matter content subjected to steaming.



**Figure 14. Effect of chip moisture content on residual air content of chips (chip length 25 mm) during steaming at 100°C /23/.**

The work by Malkov and Kovasin et al. gives a good idea why there were no dramatic improvements from the Va-purge treatments in the 1950's and why, as pulping temperatures were lowered in pursuit of a modified pulping process, the question of air removal again became important. The reason is simple and is aptly illustrated by Figure 15 showing the floating tendency of chips under various combinations of pressure and chip dry matter content.





**Figure 15. Density of penetrated chips as a function of dry solids and degree of penetration /5/.**

At the high pulping temperatures used in the 1960's (~170°C), the pressure in pulping was so high (>7.9 bar) that any residual air in the chips was compressed to a very small volume. This meant that the incremental benefit of efficient air removal was very limited. The biggest benefit would have come from reduced non-uniformity in delignification, but at the time the possibilities of measuring this effect would have been quite limited. It was not until process temperatures were significantly lowered that the air content in chips became a problem. When process temperatures (and thereby pressures) were lowered in digesters with insufficient air removal, the end result was runnability problems, caused by chips that would float in the digester. This led to the introduction of more efficient steaming vessels which eliminated the problem. In general, the importance of steaming is well understood today and current installations provide good enough steaming prior to impregnation.

These effects have been studied by Kleinert & Marraccini /24/ who found that rejects and lignin content were lowered when penetration was improved by applying high pressure in impregnation. Adding surfactants had a slight negative effect on impregnation (alkali uptake and pulping results). Similar results were achieved by Malkov et al. /25/ when they studied the uniformity of delignification in pulping with varying front-end treatments. Further work by Malkov et al. /26/ showed that optimizing the front-end treatment of chips reduces rejects somewhat and can lower the kappa number by 5-10% at the level of kappa 30. No differences in papermaking properties were found. Basically, it seems that poor air removal and impregnation will lead to non-uniformity in pulping, but the lignin content cannot be reduced very much by optimal pre-treatment. Or put more bluntly, bad air removal will destroy digester runnability, but the benefit of perfect air removal for pulping speed is not very big.

### 2.3.2 Intensification through improved diffusion

Studying the impact of alkali diffusion on kraft pulping is made complicated by the fact that there is always some consumption of alkali during diffusion. The alkali-consuming reactions become more pronounced with increasing temperature, as explained in section 1.2.2. To make the concepts somewhat more clear, the following discussion on diffusion is divided into a discussion of diffusion at impregnation temperatures (<120°C) and at cooking temperature (>130°C).

Diffusion depends on the random movement of molecules. The particle flux in diffusion is described by Fick's law:

$$J = -D \frac{dc}{dx} \quad \text{Equation 2}$$

In other words, diffusion is proportional to the concentration gradient ( $dc/dx$ ) and the diffusion coefficient ( $D$ ).

The diffusion coefficient follows the Einstein equation in which the coefficient of diffusion can be written as:

$$D = \frac{kT}{f} \quad \text{Equation 3}$$

where the frictional force on the particle ( $f$ ) can be described by Stoke's law, thus giving the Stokes-Einstein equation for diffusion:

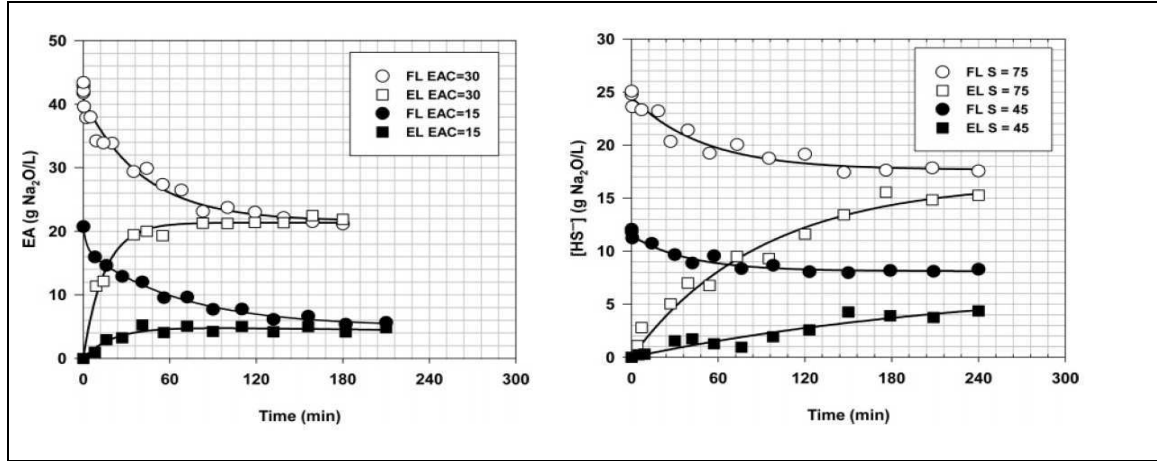
$$D = \frac{kT}{6\pi\eta a} \quad \text{Equation 4}$$

where  $a$  is the effective particle size and  $\eta$  is the viscosity of the liquid that the particle travels through. In other words, an increase in viscosity makes ionic diffusion slower. An increase in temperature on the other hand makes it faster.

Diffusion can be increased in three ways in kraft pulping:

- by increasing the driving force (concentration gradient),
- by increasing the speed of the molecules (temperature)
- by decreasing the friction affecting the molecules

A source of complication for diffusion in kraft pulping is that there are two species of ions that are important and which behave rather differently. The hydroxide ion diffuses rapidly in alkaline environments as it can move through charge transfer. The consumption of hydroxide is also great and very temperature-dependent in the kraft pulping system. On the other hand, the hydrogen sulfide ion diffuses much slower and is not consumed to any major extent in kraft pulping. The difference between the two ions is illustrated in the graphs in Figure 16.

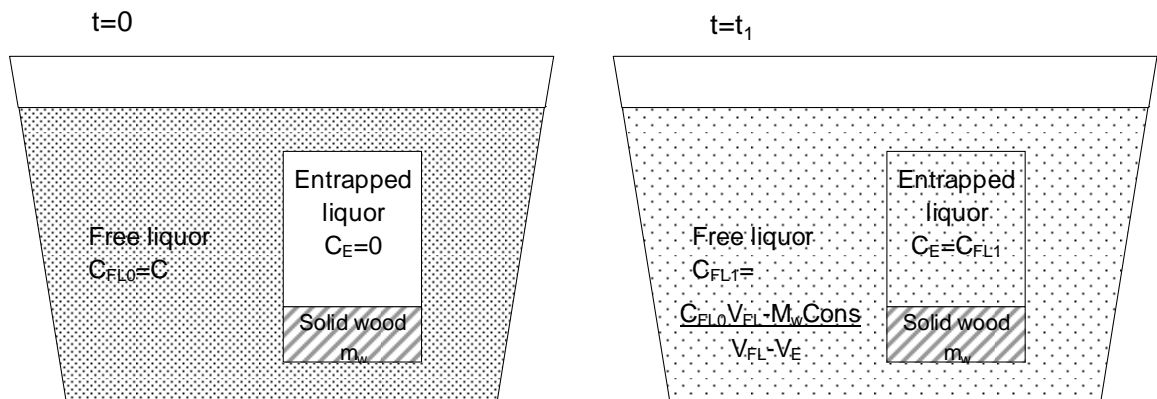


**Figure 16. Effective alkali concentration profiles in free (FL) and entrapped (EL) liquor for different initial effective alkali charges (EAC, g Na<sub>2</sub>O/100g wood, sulfidity 30%) (left) and hydrogen sulfide ion concentration profiles for different sulfidities (S,%, EAC=15) (right) Eucalyptus globulus wood, 165°C /27/.**

The above results refer to hardwood, but the principle is clear. The alkali concentration in entrapped liquor pressed out from the wood after a given reaction time reaches its peak level after only about 60 minutes. For hydrogen sulfide it takes nearly three times as long. This points to very different diffusion characteristics of the two ion species.

In this discussion, emphasis will be put on the transfer of hydroxide, as no kraft pulping can take place without it. In the absence of better knowledge, it is assumed that sufficient concentrations of hydrogen sulfide are present when impregnation has been thorough.

A further problem is the fact that alkali is consumed in different reactions starting at very low temperatures. This means that the concentration inside the wood is dependent both on the amount of alkali that has diffused and the amount of alkali consumed in the reactions. To quantify these parameters the concepts of alkali uptake and wood alkali consumption can be used.



**Figure 17. Schematic representation of free liquor, entrapped liquor and solid wood in impregnation studies with impregnation time  $t_1$ . Wood model as presented in figure 13.**

$$\begin{aligned}
\text{Alkali uptake} &= \text{Loss of alkali in free liquor} \\
&= \frac{V_{FL} \times C_{FL0} - V_{FL1} \times C_{FL1}}{m_w}
\end{aligned}
\tag{Equation 5}$$

$$\begin{aligned}
\text{Wood alkali consumption} &= \text{Alkali uptake} - \text{Entrapped liquor alkali} \\
&= \frac{V_{FL} \times C_{FL0} - V_{FL1} \times C_{FL1}}{m_w} - \frac{C_E \times V_E}{m_w}
\end{aligned}
\tag{Equation 6}$$

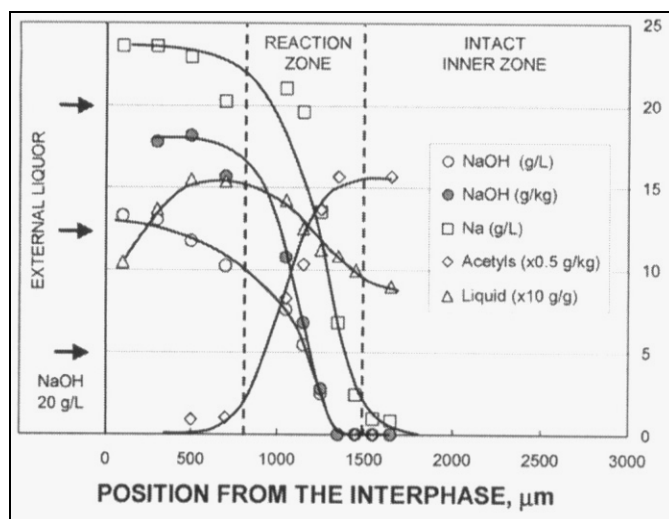
As indicated by the equations above, wood alkali consumption can only be determined by leaching out the alkali in the entrapped liquor or by otherwise acquiring a representative sample of the concentration inside the wood.

### 2.3.2.1 Diffusion in impregnation

Unlike penetration, diffusion in impregnation involves a lot of open questions. The biggest question regards the amount of chemicals that should be transferred during the impregnation stage. As a minimum, there should be enough alkali to cover the reactions that take place during the impregnation stage, thus maintaining alkaline conditions in the entrapped liquor. There are different views on the impregnation from there onwards, and on the benefits of different ratios of OH/HS ions. The present discussion will, however, focus on the impact on overall pulping speed of various modes of impregnation. A problem in this context is that impregnation generally is seen only as a way to avoid uneven pulping (rejects). The impact of impregnation on aspects such as pulping speed and process yield is more rarely commented on.

Several researchers have examined the diffusion in wood. The work by Hultholm et al. /31/ gives the amount of alkali taken up by the wood as the difference between alkali charged and alkali that can be leached out post-impregnation = wood alkali consumption. Other researchers have tried to measure the concentration of liquor inside the wood /3/ and also quantify the de-acetylation-consuming alkali during impregnation /28/.

A very illustrative way of studying the advance of impregnation has been used by Zannutini et al. /29/ for eucalyptus. Their results concur with those of Hultholm et al. as to the fact that the most important factor for the progress of impregnation is the concentration of the impregnation liquor, not the impregnation temperature. They also show the impregnation profile as a clear S-shaped curve in the wood cross section, indicating a clearly separated reaction layer that is moving into the chip. The concentration of sodium in the reacted zone is close to that of the surrounding liquor, whereas the concentration of hydroxide is significantly lower. The difference is thought to be due to the competition between hydroxyl ions and the anions created by the reaction with wood. This can be seen in Figure 18 for eucalyptus wood.



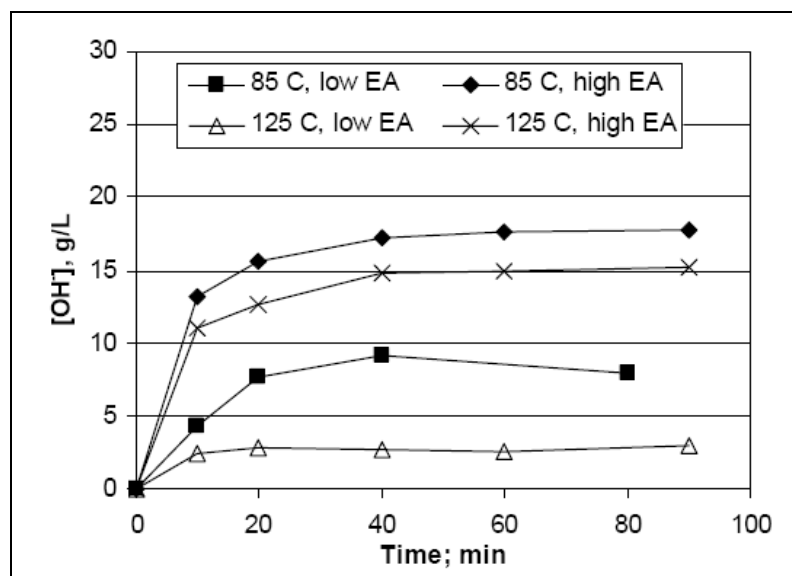
**Figure 18. Profiles of alkali impregnation of fresh eucalyptus wood. (Alkali content as g NaOH per kg of oven dry (o.d.) wood, acetyl group content as x 0.5 acetyls per kg of o.d. wood and liquid content as x 10g liquid per g of o.d. wood) /29/.**

The theory that unimpregnated wood has a clear reaction zone gets more support from further work by Zanuttini et al. /30/. Their work indicates that wood behaves like a glassy polymeric solid placed in contact with a solvent. This means that at least the first wave of alkali diffusing into the wood chips cannot be modeled by simple Fickian diffusion, because the diffusion properties change as the chemical front advances. In practice, this does not change the behavior of wood in impregnation very much, but should be kept in mind in any attempt to model the diffusion in the impregnation stage.

In the following paragraphs different ways to improve diffusion in impregnation will be discussed in more detail.

### **Increased temperature**

An increase in temperature will make diffusion faster as the random movement of ions becomes faster. However, this also increases the consumption of alkali in non-delignifying reactions, eventually leading to lower yield. Several researchers have investigated the impact of temperature on impregnation results /31,10/. Research is currently being undertaken at HUT to get a clearer picture of the composition of the entrapped liquor inside the wood after impregnation. This should help to clarify the extent to which increased temperature leads to higher chemicals consumption and faster diffusion.



**Figure 19. Development of EA concentration inside fresh industrial 4-6 mm thick spruce chips during impregnation at different temperatures using 16 and 32 g NaOH/l impregnation, liquor to wood ratio 10:1 /31/.**

In Figure 19 the concentration of alkali inside the wood is calculated based on the amount of alkali that can be leached out from impregnated wood after an impregnation stage. Therefore, no consumption of alkali during the impregnation stage is considered in this approach. As seen in Figure 19, increasing the temperature is not the way to achieve a higher amount of “free” alkali (alkali that can be leached back out) in the wood. The increased consumption attached to a temperature increase in fact lowers the “free” concentration in the wood. On the other hand, the same figure clearly shows the benefit of higher concentration.

Useful additional information on yields and alkali uptake in softwood impregnation can be found in the work by Robertsen et al. /32/. In their work, the same dependence on alkali uptake is seen for liquor concentration and temperature.

**Table 3. Alkali consumption and uptake in impregnation of softwood at 80 and 120°C. 3h impregnation, NaOH concentration 1 mol/l /32/.**

Temperature	Alkali consumed kg NaOH/ton wood	Alkali uptake kg NaOH/ton wood	Total yield (on wood)	Lignin dissolved (of total)
80°C	60	120	90%	8%
120°C	100	140	<80%	25%

As can be seen from the results in Table 3, an increase in temperature increases the consumption of alkali much more than it increases the alkali uptake (= total alkali consumption).

However, when the diffusion of hydrogen sulfide is taken into account, the picture changes. The diffusivity of hydrogen sulfide is lower than that of hydroxide, and hydrogen sulfide is not consumed during impregnation in the same manner as hydroxide. For this reason, an increase in temperature during impregnation will in fact increase the amount of hydrogen sulfide transferred. Hultholm & Lönnberg

report an increase from 0.3 mol HS-/kg wood to 0.42 mol during 40-minute impregnation when increasing the temperature from 80 to 130°C /33/. These tests were, however, performed in a solution without added hydroxide ions.

In examining the effect of temperature in impregnation on intensification, a problem is that there is not very much information on the effects of different amounts of consumed alkali, free alkali and lost yield after impregnation on the actual cooking parameters. However, it does seem logical that extensive yield loss and thus alkali consumption should be avoided during impregnation, as any yield lost during impregnation cannot be recovered in later process steps.

### **Increased concentration**

As seen in Figure 16 and Figure 19, there is a very strong correlation between the concentration of impregnation liquor and the amount of alkali moved into the wood in impregnation, but the problem of knowing the effects of various levels of transfer in impregnation on the actual cooking remains. Steam phase pulping is one particular method that has been the subject of extensive research into the effects of various impregnations. One of the first researchers to really understand the importance of thorough impregnation as a means to achieve fast pulping was Kleinert in his work on “Rapid Alkaline Pulping” /10/. In this work, impregnation was performed at a high liquor-to-wood ratio (1:10 and 1:20) and a high concentration (40-80 g/l EA as NaOH), followed by fast (20 minutes, 182°C=810 H-factor) steam phase pulping. The alkali transferred to the wood and the degree of delignification achieved were in clear correlation with the concentration in impregnation, as illustrated in Figure 20 and Figure 21.

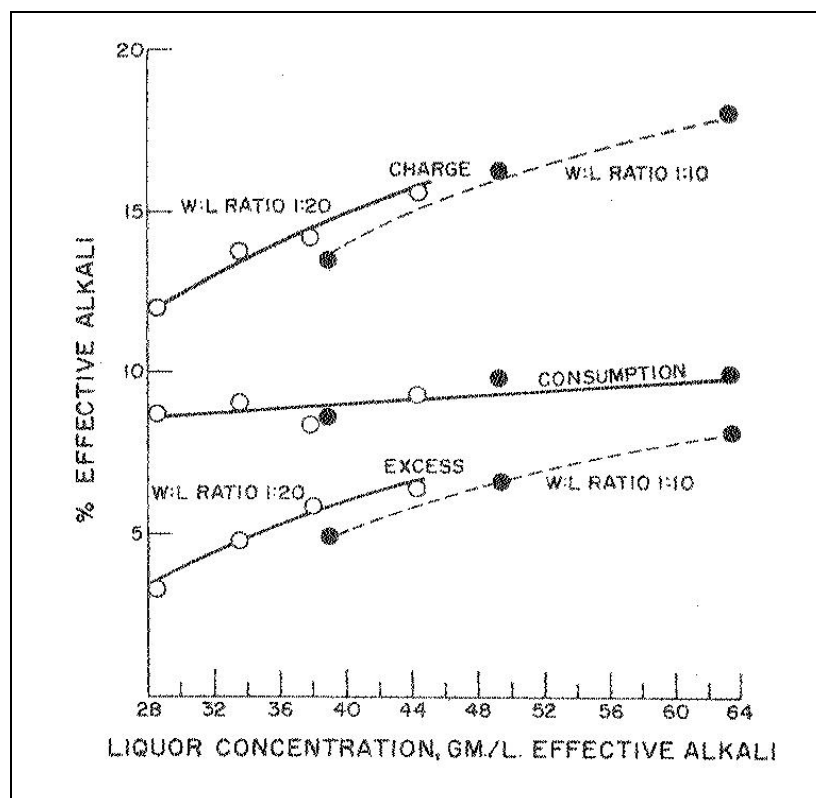


Figure 20. Charge and consumption of effective alkali in short cycle vapor-phase kraft cooking, alkali as  $\text{Na}_2\text{O}$ . Charge calculated as difference between concentration of liquor entering and liquor withdrawn after impregnation. 130°C, 20 min impregnation /10/.

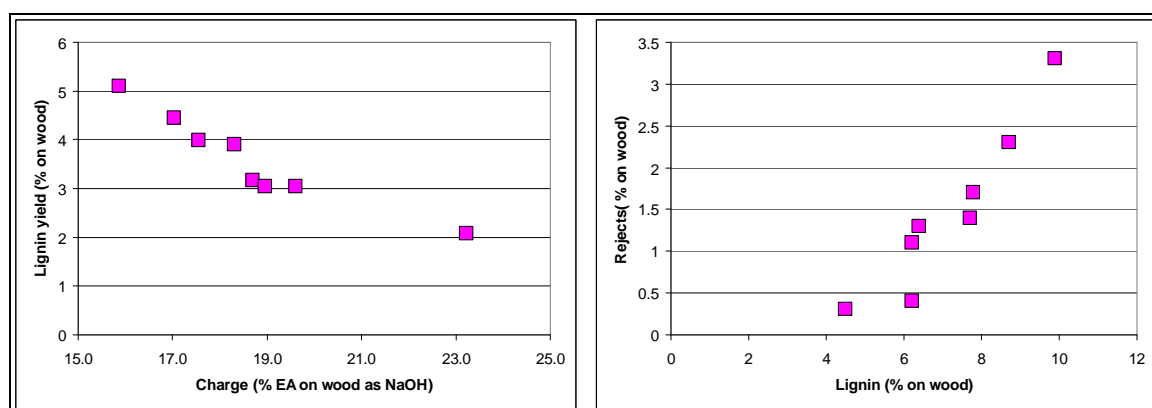


Figure 21. Results from Kleinerts work regarding attainable degree of delignification for different charges and rejects as a function of delignification. Impregnation 20 min 130°C, pulping 20 min 182°C in steam phase /34, 35/ .

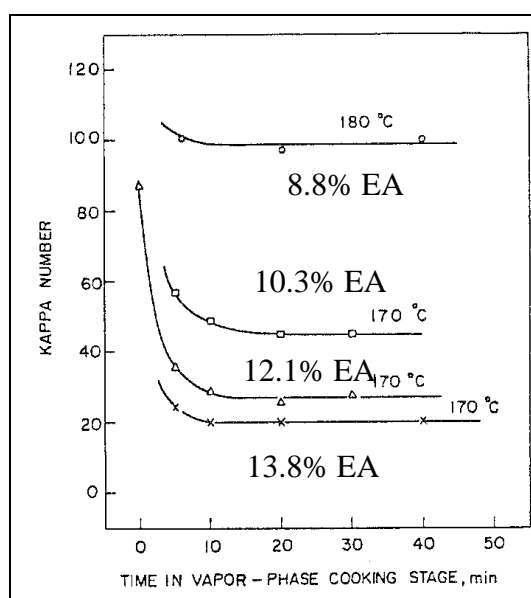
Kleinert's results show that it is possible to get fully defiberized pulp using short cooking times, provided that the impregnation has been thorough enough. The pulp yield of cooks with 1% rejects was around 50% on wood. However, an increase in excess alkali after pulping did lead to a loss of pulp strength and viscosity, as did an increase in temperature. Kleinert speculated that the mechanism of delignification in rapid cooks was one of free radicals. This claim was backed up by an article in *Nature* /36/. An added benefit of rapid alkaline pulping was a very small amount of mercaptans, and thus odor, in rapid pulping.



Production of pulp with a strength matching that obtained in kraft liquid phase pulping and with similar bleaching characteristics was claimed to be possible /35/.

The process was also tested with different wood species, indicating that it worked both with hardwoods and softwoods, but that wood density was a critical factor. High-density hardwoods needed a higher concentration of impregnation liquor because of the restricted volume of liquid that the wood can hold /37/.

Similar results have been seen in other research into processes with high liquor concentrations in impregnation. One study concerning pre-treatment of wood using sodium sulfide showed that increasing the pre-treatment concentration from 15 to 30 g/l  $\text{Na}_2\text{S}$  reduced the H-factor needed to reach a given kappa number by about 30% /38/. Other researchers have achieved similar results in studies with strong impregnation prior to delignification. One such method is the White Liquor Impregnation process (WLI) /39/. Clearly, increased concentration in impregnation can be used as a means to intensify kraft pulping.



**Figure 22. Kappa number as a function of digestion time in vapor phase pulping and alkali consumption in impregnation for beech chips (consumption as % NaOH on wood) /55/.**

The impact of different alkali transfers in impregnation can be seen in Figure 22. It is clear that delignification is very fast in the vapor phase and stops abruptly when the alkali impregnated into the wood has been consumed.

The implications of high-concentration impregnation and vapor phase and WLI pulping are discussed in greater detail in section 2.3.2.3.

### Decreased obstruction of diffusion

A further way to promote diffusion would be by expanding the effective cross sectional area inside the wood available to diffusion. In pulping terms this amounts to a removal of substrate that can hinder the free movement of molecules. The barriers to diffusion can be both physical and chemical, so a greater effective cross sectional area can be gained both by removing physical

obstacles, such as pit membranes or hemicellulose blocking access to lignin molecules, and by removing wood constituents that consume chemicals and thus slow the effective transfer through diffusion. Both pre-hydrolysis and different forms of chip leaching prior to impregnation have been proposed. Hultholm et al. /31/ suggest the use of two-stage impregnation. The idea of pre-hydrolysis can be criticized on the grounds that it probably increases alkali consumption and reduces total yield as carbohydrates are converted into acids that need to be neutralized. As such, these ideas do not constitute process intensifications.

### **2.3.2.2 Diffusion in the cooking stage**

It is generally stated that kraft pulping is not diffusion-limited as long as the cooking temperature, chip thickness etc. are kept within normal limits /40, 41/. This limit depends on the wood species and cooking conditions, with an increase in temperature drastically reducing the maximum chip thickness at which diffusion is not the limiting factor /42/. The speed of diffusion for alkali is the same in all directions during kraft pulping /20/. Kraft pulping modeling gives some ideas of the interplay between mass transfer and reactions in cooking.

Since the advent of the H-factor model described earlier, more detailed models for kraft pulping kinetics have been constructed, which take into account the effect of the concentrations of both delignifying chemicals as well as the lignin and carbohydrates in the wood. The most popular one is probably the Gustafson model that divides the pulping process into three distinct phases; initial, bulk and residual delignification /19 /. Another possibility is to divide the reactive components (lignin and carbohydrates) into different reactivity classes /43/. Combined with a model for the diffusion of chemicals into the chips, the Gustafson model is fairly accurate even at predicting non-uniformity in pulping. However, it still makes no attempt at explaining the actual reactions in kraft pulping but is instead based on a black-box approach to the overall reactions. Also, there seems to exist some uncertainty about the numerical values of several of the parameters. For instance the Gustafson model uses an activation energy for diffusion in hardwood of 20.4 kJ/mol, whereas others have measured figures as low as 1.24 kJ/mol /44/.

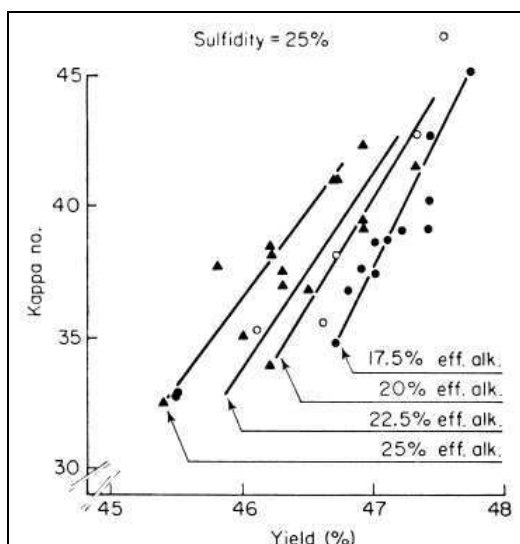
The same possibilities exist as in the impregnation step, i.e. increased temperature, increased concentration and a shortened diffusion path to increase diffusion.

#### **Increased temperature**

As discussed in the section on pulping temperature 2.2.2, the range of movement in temperature is limited due to formation of rejects. If the cooking temperature is increased very much, there will be more rejects as the rate of reaction increases faster than the rate of diffusion.

#### **Increased concentration**

Clearly the easiest way to increase pulping speed is to use a higher charge of pulping chemicals. This, however, leads to lower process yield if performed in a conventional cook, as seen in Figure 23.



**Figure 23. Total yield vs. kappa number with various alkali charges in conventional pulping /5/.**

A high cooking chemical charge also adversely affects pulp viscosity, which has been the main focus of research into so called modified pulping. The results of this research have emphasized the use of as low charges and as even concentration profiles as possible. Also, on an industrial scale, it clearly is beneficial to use as little chemicals as possible. Due basically to these reasons, the common understanding in modern kraft pulping is to use as little chemicals as possible, while maintaining a level where there still is some rate of reactions. The importance of brownstock pulp viscosity was touched upon in section 2.1.

An interesting fact is that a high alkali charge will not only lead to a short cooking time but also to a high amount of  $\beta$ -O-4 structures in the unbleached pulp. In bleaching sequences based on oxygen and peroxide, a high remaining amount of  $\beta$ -O-4 structures has been shown to be advantageous, since hydrogen peroxide will oxidatively degrade such structures, resulting in enhanced fragmentation of the lignin /45/. The fact that the chemicals charge, cooking time and lignin structures are interdependent indicates that the availability of chemicals inside the wood is non-uniform, implying that kraft pulping may indeed be mass transfer-limited.

### Shortening the diffusion path

In kraft pulping, the diffusion speed is of about the same order of magnitude in all chip directions /20/. This means that, as chip thickness is more than one order of magnitude smaller than chip length, chip thickness is the critical parameter for mass transfer by diffusion. Thus, the diffusion path of pulping chemicals can be shortened by reducing chip thickness. Trials with thinner chips have shown benefits in pulping speed and uniformity. The knowledge that chip size is a determining factor for the outcome of pulping is by no means new. As early as in the 1950's it was shown that chip shredding gave 40% faster pulping and much lower rejects levels /20/. Similar results have been registered for thickness-screened chips in industrial cooking. Thickness-screened chips gave lower kappa numbers, higher total yield and lower rejects than plate-screened chips /18/.

In general, in mill installations thinner chips are not an option, as the thickness and chip length produced by industrial chippers are dependent on each other and thinner chips lead to shorter chips and thus cut fibers. Also, very thin chips can be difficult to process in current digesters designed for a certain chip shape, in addition to which chipper yield decreases when producing small chips. Thus, the potential for process intensification through the use of thinner chips is limited.

### **2.3.2.3 Pulping methods with superior impregnation**

Based on the discussion of diffusion in impregnation and cooking it is clear that any significant increase in mass transfer has to take place at lower temperatures to avoid excessive yield loss. There are two processes that utilize this principle, namely steam phase pulping and the WLI process. Some of the aspects surrounding these processes are discussed in the following.

#### **Mass transfer**

A basic difference between the two processes is that in steam phase pulping all mass transfer has to happen in the impregnation step. However, there can be some mass transfer between the chips, as shown by Ahlgren & Olausson /59/. They studied the impact of uneven impregnation prior to vapor phase pulping. They impregnated part of the wood with all of the chemicals needed for the cook and the rest was left completely unimpregnated. By varying the ratio of impregnated to unimpregnated chips and the impregnation concentration, the researchers were able to have a constant alkali uptake but cooks with very different impregnation characteristics. The result was that using slow heat-up (1°C/min 70-170°C) the whole load of chemicals could be packed into 50% of the chips without affecting the overall delignification characteristics. Strength characteristics were, however, affected by uneven impregnation. Based on these results, it seems that steam heating actually forms a liquid film on the wood that makes alkali transport possible between chips. Also, in steam phase there is a very limited volume for dissolved wood constituents to disappear into. This can be an explanation for the higher yield observed in these cooks. The dissolved hemicelluloses do not have anywhere to go and are thereby to be re-grafted to the fibers, even if they may have been dissolved to some extent earlier in the process.

In WLI pulping there is a normal liquor phase in the digester. This might lead to a situation where some of the chemicals present in the wood can actually leach out, making the final cooking slower than what would be expected based on the impregnation.

#### **Pulping speed**

Steam phase pulping is faster than WLI and batch kraft pulping. According to Jokela /39/, the H-factor needed in WLI pulping is about the same as in conventional batch kraft pulping.

#### **Rejects**

Both steam phase and WLI pulping have low rejects for a given lignin yield. This is probably due to uniform cooking thanks to thorough impregnation.

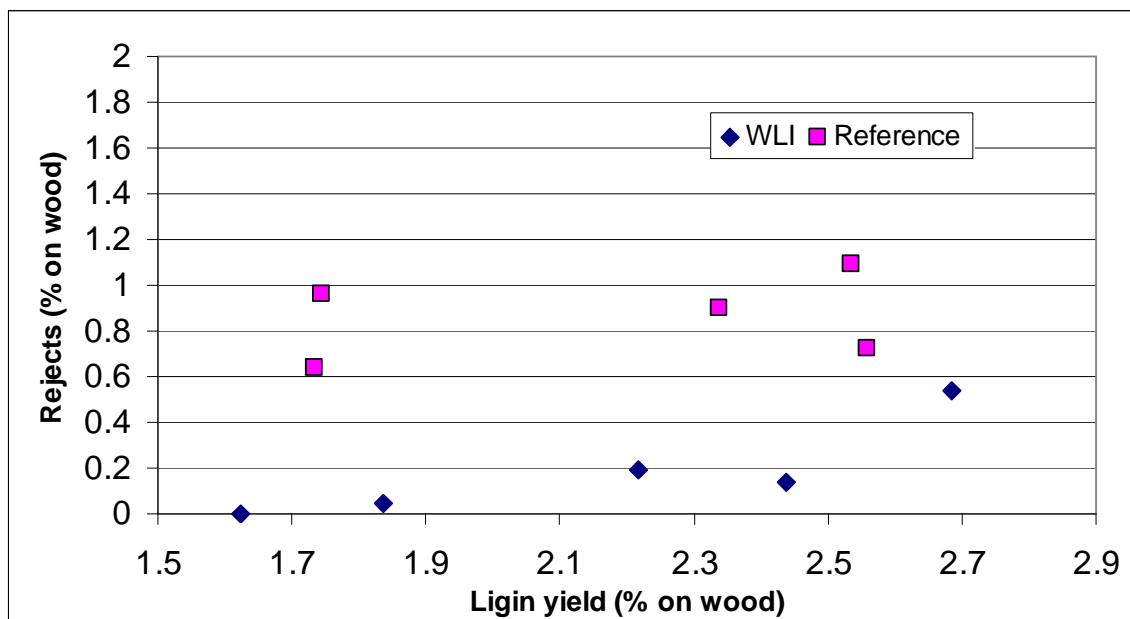


Figure 24. Rejects vs. kappa number in WLI and one-stage batch kraft pulping (Reference). Drawn from Jokela's own data /39/.

The rejects levels of vapor phase pulps shown in Figure 25 also highly resemble the results for WLI pulping in Figure 24. The results indicate uniform delignification through the whole chip even at rather high lignin contents. A curious thing is that the rejects at kappa 30 seem higher for vapor phase than liquid phase pulping. This may, however, merely be due to natural variation in the experimental procedure.

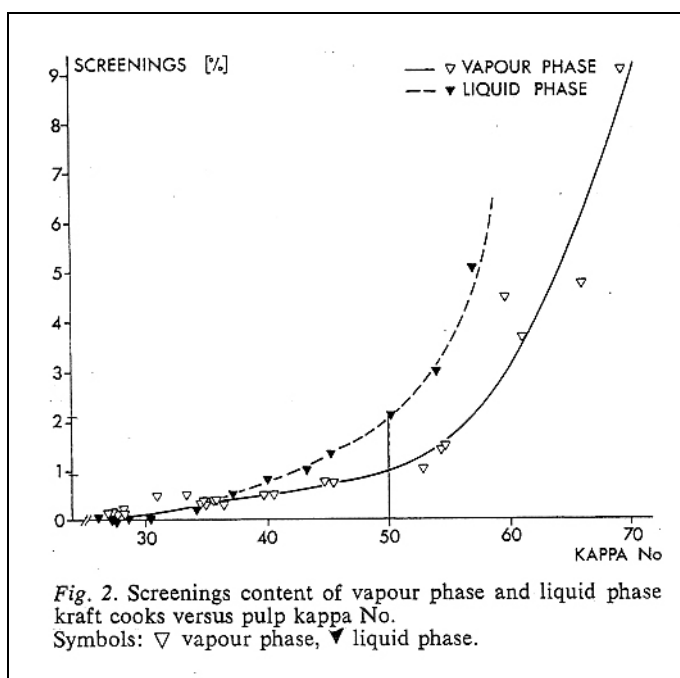
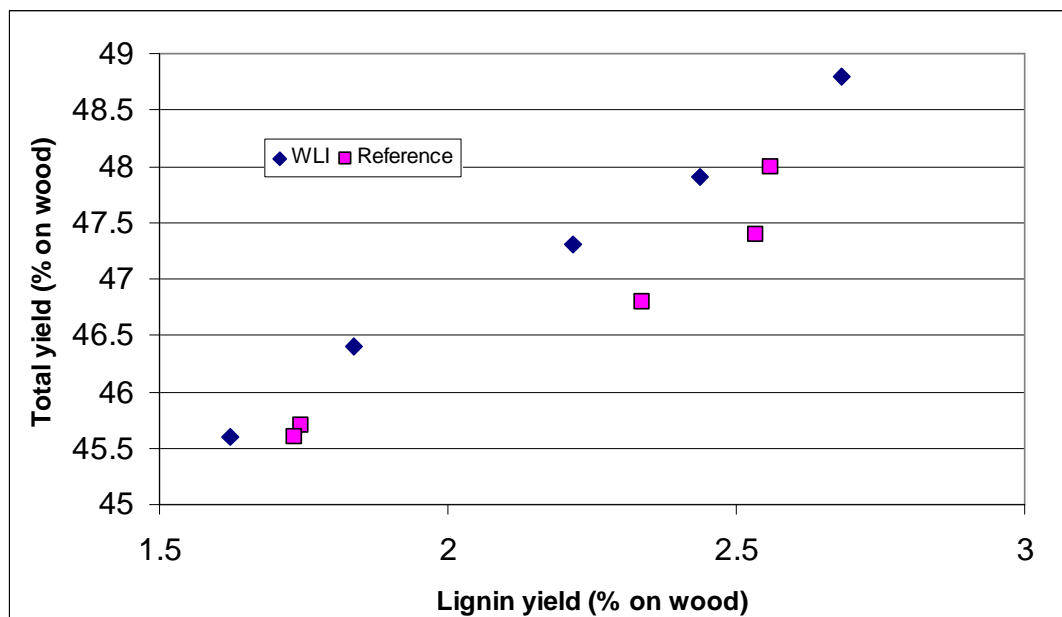


Figure 25. Rejects vs. kappa number for vapor phase and liquid phase pulping of 20x20x3mm pine chips /60/.

To further study the origin of screen rejects in vapor phase pulping a study was performed in which softwood earlywood and latewood were pulped separately /46/. The results clearly showed that latewood pulping demands a much higher alkali charge than earlywood. In liquor phase pulping this problem is solved by using a long residence time and diffusion, in vapor phase pulping there can only be diffusion between the two types of wood, not between the wood and the liquid phase.

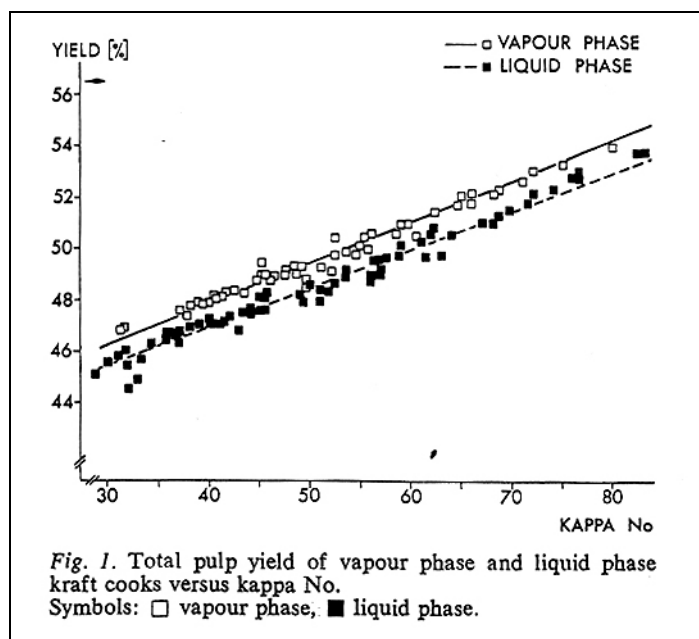
## Yield

The total yield for WLI pulping is higher than for the reference batch kraft pulping, as seen in Figure 26. This contradicts the claims that alkali concentration should be kept low in the initial part of the cook in order to achieve high yield. The benefits claimed for the WLI-Enerbatch process include higher yield, lower rejects and the possibility to use lower-value wood as raw material thanks to the efficient impregnation. In addition, the fact that the digester content is cooled down to under 100°C before blowing the digester is claimed to reduce emissions of mercaptans and other odorous sulfur compounds. The concentration in impregnation is 65-70 g/l Na<sub>2</sub>O /47/. This leads to a short cooking stage, and thanks to displacement heating using hot liquors from previous stages, steam savings of up to 60% compared to conventional batch pulping are reportedly achieved.



**Figure 26. Total yield vs. kappa number for WLI and one-stage kraft pulping (Reference). Drawn from Jokela's own data /39/.**

In the same way as the results for the WLI pulping, the results for vapor phase pulping yield seen in Figure 27 are also quite difficult to explain based on the so-called rules of modification for kraft pulping. The concentration profile of the cooks is very steep and the concentration of dissolved material inside the chips must be substantial towards the end of the cooks. Still, the yield is very good.



**Figure 27. Total yield for vapor phase and liquid phase pulping of 20x20x3mm pine chips /60/.**

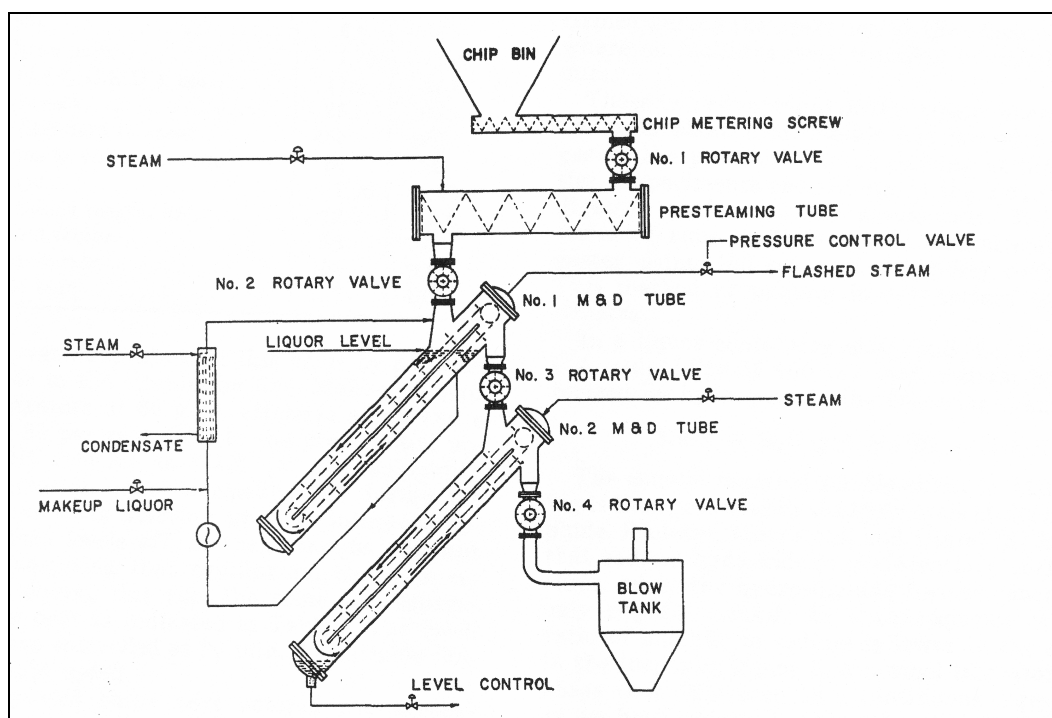
The work of Kleinert and others in the 1960's showed that an intensified pulping process could be achieved through the use of vapor phase pulping. Characteristic of vapor phase pulping is that impregnation has to be performed using high concentrations to ensure that sufficient amounts of pulping chemicals are present in the wood prior to the cooking stage. This is obvious, as no bulk liquid is present to work as a buffer of chemicals.

Kleinert /48/ took the whole idea of vapor phase pulping to the extreme, going as far as to make trials where wood meal was first impregnated with alkali and then dried before being subjected to heating using superheated steam. This essentially constitutes heating under completely dry conditions. The result was very rapid lignin cleavage without any signs of the different stages of delignification that generally are described in kraft pulping kinetics (initial, bulk and residual delignification). The carbohydrates were naturally severely damaged by the harsh treatment, but the tests clearly showed that the liquid phase as such is not needed in alkaline delignification.

#### **2.3.2.4 Industrial history of steam phase pulping**

The earliest trials using vapor phase pulping date back at least to experiments with Va-Purge impregnation /49/. These mill-scale experiments were performed in batch digesters, so the benefit in terms of process time was not very big (the filling and heat-up of the digester took so much time that the benefit of a fast reaction stage remained small). Savings in steam consumption where, however, registered. Research into different aspects of vapor phase pulping was quite active while the interest lasted. Much of the work was performed in Canadian research institutes. The work on vapor phase kraft pulping in Canada in the late 1950's and early 1960's culminated in a series of patents /50, 51, 52/ describing both the equipment and the high-sulfidity process used and both pilot- /53/ and mill-scale operation of vapor phase digesters.

The Canadian system that operated at mill scale was run by re-circulating the impregnation liquor, leading to accumulation of sulfur in the system (Figure 28). The process with 100% sulfidity was claimed to give excellent pulp strength and low alkali demand and was dubbed the alkafide process. The mill-scale system was a 150 ton/day digester at Domtar Newsprint Ltd in Canada. The plant was claimed to have a residence time from steaming to bleachable grade pulp of just 40 minutes and an alkali consumption of only 65-75% of that of batch pulping to the same lignin content /54/.



**Figure 28. Schematic layout of vapor phase digester and liquor circulations /53/.**

### Benefits

The following advantages were claimed for rapid pulping in vapor phase /54/

1. Lower chemical and steam costs
2. Higher pulp quality
3. Smaller in-process inventory
4. Lower capital cost per ton
5. Reduction of odor due to virtual elimination of mercaptan formation

Also, the small in-process inventory made the continuous digester very flexible. Starting from an empty digester, good-quality pulp could be produced within an hour, a performance unparalleled by modern cooking plants /53/.

At the same time with the work in Canada, Japanese researchers were working on the concept of alkaline vapor-phase pulping /55/. Their work centered on hardwood pulping and showed much of the same characteristics as that of the Canadians, namely high sulfidity and high impregnation temperature. The researchers realized that the impregnation step is a combination of physical impregnation and chemical reactions. Trials were also performed on pilot scale (0.5 ton/day) /56/. The use of liquor circulation during impregnation gave a clear advantage by making it possible to use a very high



effective liquor-to-wood ratio, ensuring high concentration inside the wood without the need for an excessive maximum concentration. This also led to very high sulfidity, which was seen as beneficial in cooking. The pilot plant gave higher yields than the same process performed in an autoclave system, possibly due to lower impregnation concentration or because carbohydrates lost in impregnation stayed in the system when re-circulating the impregnation liquor in the pilot plant system.

### **Problems:**

As is evident when looking at the digester base installed today, vapor phase pulping never caught on industrially. The 150 ton/day digester installed at Domtar Ltd. was intended as a demonstration unit for bigger installations in the future (normal mill size was around 600 tons/day at that time) /57/. The benefits in terms of chemical savings and yield benefits were not so big at industrial scale as was to be expected from laboratory trials. Also, the amount of rejects was higher than expected, possibly in part due to bad chip quality.

Problems encountered in the industrial vapor phase pulping system included /57/:

- The high-sulfidity (alkafide) process was impractical, sulfur disappeared from the system in recovery.
- The mill used sawmill chips, which tended to be too thick for good impregnation, leading to high rejects.
- The digester design was not optimal; although things worked on small scale the problems became too big with scale-up. The digester problems included:
  - wear on mechanical parts, the insides of the digester had to be completely changed 3 times in 20 years
  - the impregnation would have needed good liquor circulation, which was not achieved due to extensive plugging of the screens in the impregnation stage
  - there was a high concentration of dissolved solids in the impregnation stage. This led to decreased delignification or the need to use even higher charges of chemicals as the dissolved solids consumed available alkali
  - severe scaling of heat exchangers, both organic and calcium scales were worse than those observed in continuous Kamyr digesters.
- The advantages of vapor phase pulping turned out to be smaller than expected, the advantage in chemicals consumption was not as significant as expected, the smaller energy input needed was upset by new generations of continuous digesters having better heat recovery, the odor problem was reduced (mercaptans down by 50%) but not completely eliminated

Vapor phase pulping was not a complete failure, though. The Domtar digester was producing vapor phase pulp from 1965 to 1972, and was then converted to liquor phase sawdust pulping and was used until 1995.

An important reason for the shortcomings was probably the excessively high impregnation temperature, which was not seen for what it really was, i.e. a short conventional liquid phase cooking step at high concentration. This would certainly explain the accumulation of dissolved solids in the impregnation step and the problems

with calcium scales. There were perhaps hopes to reduce non-uniformity by more efficient impregnation (higher temperature and longer impregnation), which in the end did not work out. In addition, there was a complicated recovery process with non-combustive oxidation etc. An underlying reason for the choice of a high temperature in the impregnation step may have been a desire to keep the temperature and thereby pressure difference between impregnation and cooking stages as small as possible in continuous operation. This thinking may have led to problems with impregnation and thereby cooking.

### **Later developments**

In the 1970's, the idea of vapor-phase kraft pulping lived on in some installations mainly designed for high-yield pulping /58/. A few more scientific papers were also presented on the subject /59, 60/ dealing with the effect of impregnation on kraft vapor phase pulping of softwood. This research showed a 1-percentage point yield advantage thanks mainly to better xylan retention, low rejects and lower alkali consumption. On the whole, however, it seems that the interest in the pulping world had shifted away from this experimental process, and continuous liquid phase pulping, which had been introduced somewhat earlier, went on to become the dominating pulping method.

In modern pulping installations vapor phase technology lives on in some continuous digesters with a short vapor phase stage in the upper part of the digester. In these digesters the vapor phase is used to achieve fast heat-up of the chips to cooking temperature. The heat-up stage is followed by liquid phase cooking. The impregnation before heat-up is insufficient to achieve considerable delignification in the vapor phase, but heat transfer is very efficient. The vapor phase part of the digester has to be kept reasonably small, because a big difference between the levels of the chip pile and the liquid level in the digester leads to severe compaction in the digester and thus loss of product quality and digester runnability.

Some new research into vapor phase pulping was conducted in the 1990's in connection with the interest in modified pulping. These studies /61/ showed that dividing the alkali charge over an initial vapor phase stage and a subsequent liquid phase stage increases pulp viscosity but gives the same yield as when charging all the alkali in the initial vapor phase stage. Increasing the alkali charge in the liquid phase stage was also found to lead to a clear reduction in yield and pulp viscosity. The experimental setup differed from the industrial steam/liquor digesters in use as the chemical charge ahead of the steam phase step was more than half of the total chemical charge.

Bofeng also studied the effect of re-circulating the impregnation liquor in the impregnation step of vapor-liquid phase pulping /62/. No impact on pulping speed was detected when the same impregnation liquor was re-used five times (air-dried softwood, H 3000 kappa 25, 46,2% yield). Preliminary mass-balance calculations show that an ordinary recovery system could supply the chemicals needed to maintain sufficient impregnation liquor strength.

Cooking with very low liquor-to-wood ratios has been used commercially in sulfite pulping. A good reference for both laboratory- and industrial-scale work is

the licentiate's thesis work of Pirkko Molketin-Matilainen /63/. An advantage of sulfite pulping is that the amount of chemicals transferred in impregnation can be more easily increased than in kraft pulping, where the recausticizing technology sets the upper limit for the achievable concentration of white liquor.

### **2.3.3 Improving the removal of reaction products**

As the aim of kraft pulping is to remove the lignin, it is clear that increasing the rate of removal of lignin fragments from inside the wood could be expected to have an effect on the overall cooking speed, i.e. resulting in intensification of the process. In connection with research into modified pulping this has been presented as a potential way to improve the selectivity of delignification. There are several variations of modified pulping. The one focusing on removal of dissolved solids from the cooking liquor is called the Lo-Solids process. This process has been used on industrial scale in several applications. As such, the aim of Lo-Solids pulping is not to intensify kraft pulping, but published results show that this aspect does exist. Maroccia & Jiang /64/ for example reported a 5 to 10% decrease in blowline kappa number when moving to Lo-Solids pulping in digesters that used modified continuous pulping.

It is also claimed that a high ionic strength makes pulping slower and decreases the bleachability of the resulting pulp /45/. In practice, it can be hard to get a very low ionic strength in industrial pulping, as liquors have to be re-used as much as possible to minimize fresh water usage.

## **2.4 Intensification through changes in pulping reactions**

The objective of all chemical pulping is to free the wood fibers by breaking enough bonds in the 3d structure of the lignin macromolecules in the middle lamella holding the fibers together. The reactions in kraft pulping seem to be quite well understood and are basically ionic reactions involving nucleophiles /65/. The main mechanisms of lignin macromolecule cleavage is the break-up of  $\alpha$ - and  $\beta$ -O-4 ether bonds. Other interpretations have been raised, for instance Kleinert pointed to the presence of free radicals in alkaline delignification in wood /36/. Others have also studied this phenomenon /66/, the problem is, however, that radicals are very short lived and hard to measure in-situ. The consensus is that the reactions are due to ionization.

A possible way to intensify the kraft process would be to find catalysts for the reactions or alter the process conditions in some other way that would speed up the reactions. This study centers on the kraft process, so only additives that somehow influence the speed and extent of these reactions will be considered here. Also, no attempt will be made at explaining the complete chemical behavior of the additives. The additives can be grouped into chemicals that actively take part in the delignifying reactions and chemicals that somehow change the process conditions and thus speed up the process. Chemicals that take part in the process are additives such as anthraquinone and polysulfide. Chemicals that do not take part in the chemical processes are for instance aliphatic alcohols; their effect on pulping speed is somewhat unclear.

### **2.4.1 Intensification through the use of accelerating chemicals taking part in lignin reactions**

Among the chemicals that take part in lignin and/or carbohydrate reactions the cheapest and most widely used accelerant is the one that actually defines kraft pulping, namely sulfur. The whole process of kraft pulping is an improvement from the soda (NaOH) pulping process. Any improvement provided by further additives has to come on top of the speed-up and yield advantage achieved by the use of sulfide in the cooking liquor. By increasing sulfidity from 0% to 31% the delignification time is reduced by half for softwood pulping /5/. The effect is illustrated in Figure 10. The most natural step forward along this line of thought is the use of very high sulfidity, as proposed for instance by Munk et al. /53/. As noted earlier, this was impractical partly due to sulfur losses, but also due to corrosion on the digester when cooking with high sulfidity/57/. Also, the incremental benefit of increasing sulfidity over 35% is minimal, at least in liquid phase pulping.

The hydroxides of different metals also have different delignification characteristics, as shown by Laroque & Maas /75/. This could be due to differences in the hydration behavior of the various chemicals. The use of sodium based chemicals is, however, definitely preferred as these make-up chemicals are cheap and easy to handle.

#### **2.4.1.1 Polysulfide**

An early attempt at improving kraft pulping was made by using polysulfide. At an early stage (1946) /5/, addition of elemental sulfur to the kraft process was found to increase pulping yield. The addition of elemental sulfur gives rise to the formation of polysulfide in the cooking liquor which in turn stabilizes hemicellulose against alkaline cleavage. The problem with this approach is that if elemental sulfur is added to the process, sulfur has to be removed at some point. This makes the recovery process more complicated.

If elemental sulfur is not used, the second option for polysulfide addition is to oxidize white liquor to produce polysulfide. This means that the amount of polysulfide in the cooking liquor will depend on white liquor sulfidity, so the charge is limited to one percent on wood at best. As some thiosulfate is produced as a side-reaction of oxidation, this leads to an overall reduction in pulping speed, and the use of polysulfide will then work as a process retardant rather than an intensifier.

However, if polysulfide is combined with a high alkali charge in impregnation, as proposed by Brännvall et al., a fast process with high yield can be achieved /67/. The proposed process constitutes an extra impregnation step using both alkali and polysulfide. As long as sufficient alkali is applied in the pre-treatment, the use of polysulfide does give a faster cook than a similar pre-treatment using only alkali and sulfide. The H-factor needed to reach kappa 20 dropped by about 25% for spruce pulping /68/. What the actual chemical balance in a mill application would look like for such a process is not yet clear.

The yield benefits of polysulfide and anthraquinone are additive and possible even synergistic /69/.

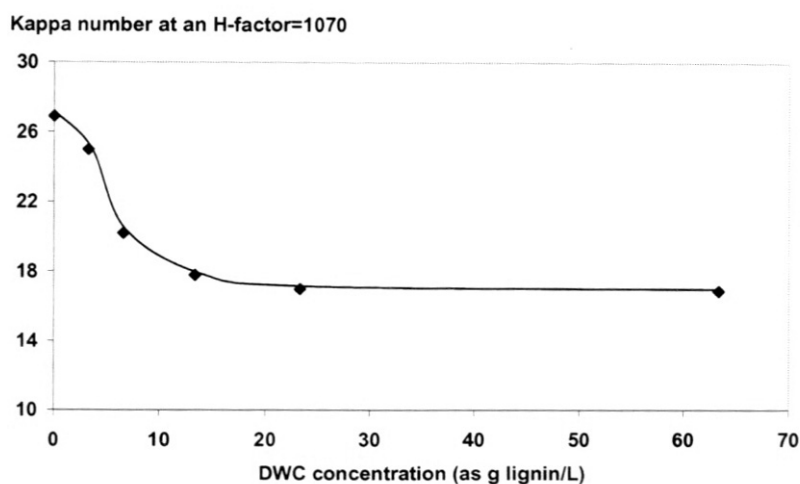
### 2.4.1.2 Anthraquinone

Another group of chemicals that has been widely investigated are different forms of quinones, mostly anthraquinone. Several related derivatives have also been investigated. Different forms of quinones have proven to be quite effective in speeding up soda pulping. The basic benefits of using anthraquinone in alkaline pulping are: acceleration of pulping and carbohydrate stabilization with yield preservation /69/. The mechanism of anthraquinone is to work in a chain of events. First insoluble AQ is electrochemically reduced by dissolved carbohydrates in the pulping liquor. The polysaccharides that give up an electron are hereby stabilized against peeling reactions. The reduced form of anthraquinone reacts with lignin by transferring an electron inducing the lignin to cleave. This oxidizes the AHQ back to AQ and the process starts over.

However, in processes with a sulfidity close to 40%, the incremental benefit on pulping speed on top of kraft pulping has not been very big /69/. For instance, addition of 0.05% anthraquinone on wood to a kraft cook reduced the kappa number by two points, if all other cooking parameters were kept constant /70/. One reason for the relatively small change compared to a kraft cook might be mass transfer. It can be speculated that the large AQ molecules may be quite slow to diffuse deep into the wood structure where the actual lignin reactions take place. For this purpose hydrogen sulfide may be more efficient. An interesting discussion of mass transfer questions related to anthraquinone pulping has been published by Samp & Li /71/.

### 2.4.1.3 Permeate from black liquor ultrafiltration

Recent research /72/ in Sweden has shown that the addition of low molecular weight lignin fractions to a softwood kraft cook increases delignification speed and yield. Under otherwise identical conditions, addition of 25%-vol of dissolved wood components to the cooking liquor caused the kappa number to drop from 34.5 to 26, compared to a cook without addition of such components. The cooks were performed as flow-through cooks. Subsequent tests indicated that it was the phenolic compounds in the dissolved wood that induced this effect. Similar results have been achieved in related work on birch /73/.



**Figure 29.** Kappa number reached at H-factor 1070 for a series of constant composition cooks of birch with different additions of industrial hardwood black liquor (DWC=dissolved wood components) to the cooking liquor and cooked under otherwise identical conditions ( $[\text{OH}^-]=0.2 \text{ mol/L}$ ,  $[\text{HS}^-]=0.2 \text{ mol/L}$  and  $[\text{Na}^+]=2.0 \text{ mol/L}$ ) /73/.

The dissolved wood component used in the study was produced by ultrafiltration of kraft black liquor. A benefit of using a black liquor based additive is that the cost of the chemical at the mill site will be low. The cost has to be calculated based on the fuel value of the organic material removed and the pumping energy needed in filtration. At mills that are constrained by recovery boiler capacity, the reduced load to black liquor combustion may actually be an advantage.

In reality, the permeate from black liquor ultrafiltration consists to a large extent of phenolic substances. It is well known that phenol can be used as a base in alkaline pulping, so the result as such is perhaps not very surprising.

#### **2.4.2 Organic solvents as accelerants in pulping**

In wood, the organic polymer lignin holds the fibers together. Identifying a simple organic solvent that would dissolve lignin but leave cellulose intact would be valuable, as in this case chemicals could be recovered simply by distillation. This is the background to work on acidic organosolv pulping by Tayenthal & Kleinert, first published in the 1930's /74/. The idea of this work was to use aqueous solutions of alcohols to delignify wood without the addition of any other cooking chemicals. The high temperatures involved lead to hydrolysis of the hemicellulose, releasing acid groups. This principle is called autocatalyzed alcohol pulping. However, the degree of delignification achievable with this method was soon found to be insufficient for commercial pulping.

Subsequent research showed that different aiding chemicals can be used to significantly improve the achievable level of delignification. Both alkaline and acidic chemicals were tested. Several chemicals are known to speed up pulping kinetics, though the way they work is not completely understood. Laroque & Maas /75/ found that the replacement of water in alkaline soda pulping by an organic solvent led to an increase in pulping speed. They attributed the increase to lower solubility of the alkali in the solvent.

Work on the acidic side eventually led to the ALCELL process, which was tried on pilot scale in Canada. The work on acidic pulping is outside the scope of this investigation and the reader is referred to one of many summaries on this subject /76, 77, 78/. In general, the pulp quality produced by such processes is poor, leading to limited commercial value, unless byproducts can be sold at high profits. After high expectations in the 1960s and 1970s that pulp could be produced on a large scale with acidic organosolv pulping, the focus slowly shifted to finding ways to provide incremental capacity for existing hardwood mills. It seems that not even this could be achieved in a commercially viable manner. The main driver was to reduce the investment cost for new installations by simplifying the recovery of chemicals.

A further variation of alcohol aided pulping is the use of alcohol in alkaline sulfite pulping. The most advanced process based on this concept is the alkaline sulfite anthraquinone methanol or ASAM process /79/. As this process uses the sulfite ion as the active lignin breaking chemical, it was left outside the scope of the present investigation which focuses on kraft pulping.

### 2.4.3 Alkaline organosolv pulping

On the alkaline side, Laroque & Maas showed an accelerating effect on alkaline pulping using various combinations of hydroxide and alcohols in their research during the 1940's /75/. Laroque & Maas assumed delignification to proceed according to a first order chemical reaction. This can be described by the equation:

$$-dL/dt = k(L_0 - L) \quad \text{Equation 7}$$

from which follows that:

$$k = 1/t \log_e L_0/L \quad \text{Equation 8}$$

where  $L_0$  is the original lignin content in wood,  $L$  is the lignin remaining after  $t$  hours and  $k$  is the velocity constant. In a series of experiments, Laroque & Maas used various combinations of hydroxides and solvent to study the speed of delignification under different chemical conditions. In Figure 30, the constant  $k$  is plotted against cooking liquor concentration for various hydroxides in different solutions.

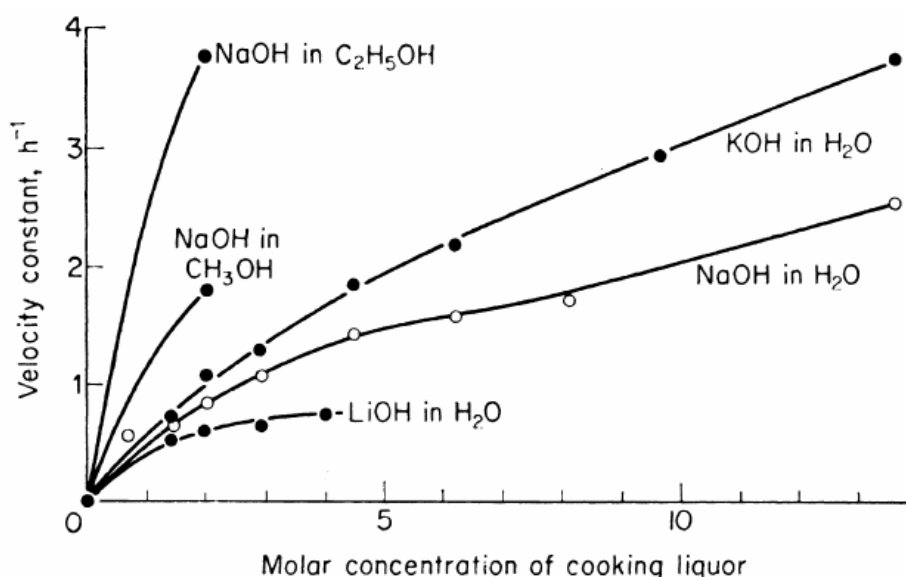


Figure 30. Velocity constant in delignifying reactions /75/.

Laroque and Maas attributed the faster pulping speed in the presence of alcohols to the difference in solubility of the inorganic chemicals in water and alcohol. Based on the fact that the change in pulping speed was proportional to the change in solubility at 25°C, they developed the concept of escaping tendency, meaning the tendency of the inorganic chemical to “escape” into the wood from the solution.

#### NaOH + alcohol

The question of alcohols in alkaline pulping was not pursued very actively until the 1980's, when environmental concerns sparked interest in sulfur free processes. Several researchers /80, 81, 82, 83/ studied the effect of alcohols on NaOH pulping of both hardwood and softwood. The process conditions used in these studies varied widely, which makes it hard to compare the setups. Some general conclusions can be drawn,

however. The pulping speed in processes with alcohols was twice as fast as in water-NaOH pulping and in some cases as fast as in kraft pulping. The process yield was reported to be up to 4% higher than in kraft pulping.

The researchers gave slightly varying explanations for the increased pulping speed. Nakano et al. /80/ used tests on model compounds to conclude that cellulose peeling is retarded and lignin condensation prevented by the presence of methanol. Nakano et al. also found that the lignin in spent liquor from wood meal pulping in the presence of methanol had low molecular weight, supporting the non-condensation theory.

Green and Sanyer /81/, on the other hand, found that solvent addition causes wood to adsorb higher concentrations of hydroxide, leading to a higher pulping rate. This is in line with the theories of Laroque and Maas. Green and Sanyer also speculated that the organic solvent may lead to better wetting of the cell wall polymers, thus leading to faster reactions. Marton and Granzow /82/ attributed the increased delignification rate of soda pulping in the presence of ethanol to lower liquor viscosity and thus better penetration and diffusion of alkali in the chips. Abbot and Bolker /83/ showed that the delignification behavior of wood in the presence of solvents is non-continuous with increasing solvent concentration. This contradicts the theory of the escaping tendency, as the solubility of the pulping chemicals decreases linearly with increasing solvent addition. Instead, the explanation was assumed to be a combination of chemical reactions and physical influence. At very high concentrations of alcohol in the cooking liquor, lignin was degraded but stayed in insoluble form on the fibers until washed with water.

#### **NaOH + AQ + alcohol**

When the use of anthraquinone as a pulping additive became more widespread in the mid-1980's, research into the combined effect of alcohols and anthraquinone was undertaken /84, 85/. The research in this field by Abbot and Bolker /84/ showed that anthraquinone and ethanol work in synergy, leading to a bigger effect than the sum of the individual effects. This was confirmed by the work of Janson and Vuorisalo /85/ for methanol, ethanol, propanol and butanol. Janson and Vuorisalo reported a yield increase of 1-4% on wood from the use of the additives, and pulp strengths close to those of kraft pulping. Also, alkali consumption was significantly reduced compared to soda pulping. A yield and speed advantage over soda and soda anthraquinone pulping of birch has also been reported when using isobutyl alcohol-water and anthraquinone as process media /86/. Isobutyl is not completely miscible in water. Abbot and Bolker suggested that the improved pulping speed is due to a change in the redox potential of the pulping liquor.

Further research into alcohol aided NaOH-anthraquinone pulping led to the development of the Organocell process in Germany and later the IDE process in Finland. The Organocell process was developed all the way to industrial scale. Originally, the process consisted of an alcohol aided pre-hydrolysis stage followed by NaOH-AQ cooking /87/. By the time when the process was implemented on industrial scale (150,000 tons/year) it had been simplified to one stage with NaOH, methanol and anthraquinone /88/. Research concerning the IDE process has been extensively reported over the years /89, 90, 91, 92, 93, 94/. The process consists of three separate stages, an impregnation stage in which wood is impregnated with NaOH, a depolmerization stage in which the impregnated wood is heated using ethanol and anthraquinone, and an extraction stage in which the cooked wood is extracted with ethanol or water. The effect on delignification in IDE pulping is much the same as that seen earlier: ethanol and anthraquinone increase pulping



speed and the process yield is 2% higher than in kraft pulping of softwood and 4% higher than in kraft pulping of birch /93/. The pulp strength is reported to be comparable to that of kraft pulp /89/.

Studies on model compounds by Brogdon and Dimmel /95/ showed that the addition of alcohol to alkaline pulping reactions increased the formation of quinone methide only if anthrahydroquinone was present. The formation of quinone methide is considered a rate-determining step in lignin cleavage, which could explain the synergistic effect of alcohol and anthraquinone.

### **Kraft + alcohol**

The interest in alcohol aided pulping has not only centered on sulfur free pulping. Some researchers have also applied alcohols in kraft pulping. A driving force behind the research has been a desire to reduce the sulfidity and thus the formation of malodorous gases in pulping. During the early 1990's, research by Johansson et al. and Norman et al. /96, 97/ showed that the speed of kraft delignification is improved by around 30% by the addition of methanol, whereas yield is improved by 1% on wood for softwood. The bleachability and strength properties of the pulps were the same as for normal kraft pulping. The 30% reduction in pulping time is confirmed by Yoon and Labosky /98/ for both aspen and spruce wood. Montplaisir et al. /99/ showed that sulfidity can be reduced by 50%, while keeping pulping speed unchanged, if a 15% methanol concentration is used in the pulping liquor. The process gave 4% higher pulp yield and a pulp with higher tear index but reduced breaking length. The research was performed on white birch. Leduc et al. /100/ verify the potential for reducing sulfidity in the pulping of softwood.

Norman et al. /97/ performed tests on cotton linters to see if the increased reaction speed was lignin-specific. They found that the attack on cellulose was also increased, but less than the increased delignification, leading to a more selective cook. In later research Norman et al. /101/ showed that the effect of organic solvents was similar for soda, soda-anthraquinone and kraft pulping. By using a wide variety of different solvents they showed that the most promising solvents were found in a narrow polarity range.

## **2.4.4 Industrial applications of solvent aided pulping**

All the research on solvent aided alkaline pulping shows that the use of solvents in the cooking stage has a clear impact on pulping speed and raises the yield. Nevertheless, Organosolv pulping has not achieved widespread industrial success.

In much of the early research in this field the cost of solvent re-generation was estimated to be too high to make solvent aided pulping economically viable /80, 85/. Growing concerns over the environmental impacts of pulping led to renewed interest in solvent aided pulping in the late 1980's. At this stage, the Organocell process was running in a demonstration plant in Munich with a capacity of 5 tons/day /76/. At the same time, a demonstration plant employing the acidic ALCELL process was being built in Canada /78/ and another employing the ASAM process at Feldmühle in Germany /88/.

The Organocell process reached commercial scale in 1991 when an old sulfite mill was converted to run with the alkali-methanol-AQ process. Production at the mill started in late 1992. Although the process did work more or less as intended, there were severe problems with reliability and pulp quality. Much of the problems with pulp quality can be

traced back to the raw material used and the lack of time for process optimization. For example, there were rather wide fluctuations in process parameters during operation, leading to uneven pulp quality. There were plans to start operations by producing fluff grade pulp, while addressing the strength problems, and then move to paper grade pulps /102/, but in the end the owners ran out of money. In 1993 the company went bankrupt and production at the mill was stopped /103/.

The other solvent pulping methods have suffered a similar fate. The ASAM demonstration plant was closed after Stora bought the Feldmühle plant /88/. The ALCELL mill was closed after 10 years without any scale-up to full production, and it has now been dismantled /104/. Its profitability was dependent on the sale of by-product chemicals, but a market for such chemicals never emerged /88/.

A lot of work has also been performed on non-wood pulping, examining the addition of organic solvents. This is outside the scope of the present research. For a list of recent references, for instance /105/ can be used as a starting point.

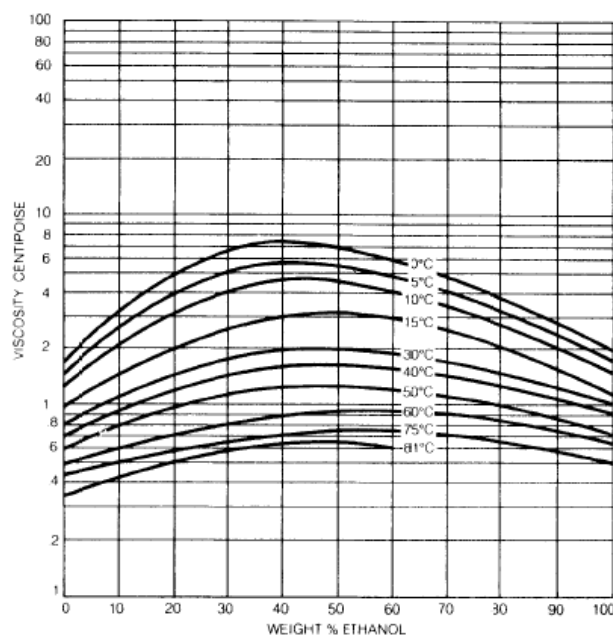
#### **2.4.5 Effect of solvents on properties of cooking liquor**

When attempting to intensify kraft pulping by adding an extra chemical to the system it is very important to understand what the chemical does to the properties of the solution. The addition of an organic solvent to an aqueous solution of inorganic chemicals such as alkaline cooking liquor has some interesting effects on the properties of the solution. The addition can affect the physical properties of the liquor as well as the chemical activity of the inorganic chemicals. The first question is that of solubility of the solvent itself in water. Generally, only organic compounds that are miscible with water have been used, but some research has also been performed with immiscible compounds. The shorter chain length alcohols such as methanol, ethanol and propanol are miscible with water, whereas longer chain alcohols are not. This study centers on miscible alcohols. Some studies have been performed to compare the effect of different solvents. In one such study on soda anthraquinone pulping, methanol, ethanol, n-propanol, i-propanol, n-butanol, s-butanol, i-butanol, t-butanol and n-pentanol were all found to have similar effects, except pentanol, possibly due to low miscibility of pentanol in water /85/.

Many of the characteristics of pulping liquors are poorly known even at low concentrations at room temperature. For alkali solvent systems the situation is even worse. Most information is on pure solvents and very limited information is available on water-solvent mixtures even at low temperatures. Knowledge about how solvent-water systems with inorganic chemicals behave at higher temperatures is non-existent.

What is known, however, is that liquid viscosity increases when alcohol is added to an aqueous solution. The viscosity has a maxima at around 40% alcohol by weight, as can be seen for ethanol in Figure 31. This leads to issues related both to penetration and diffusion and indicates that diffusion in pulping liquors should be retarded by the addition of alcohol to the liquor.

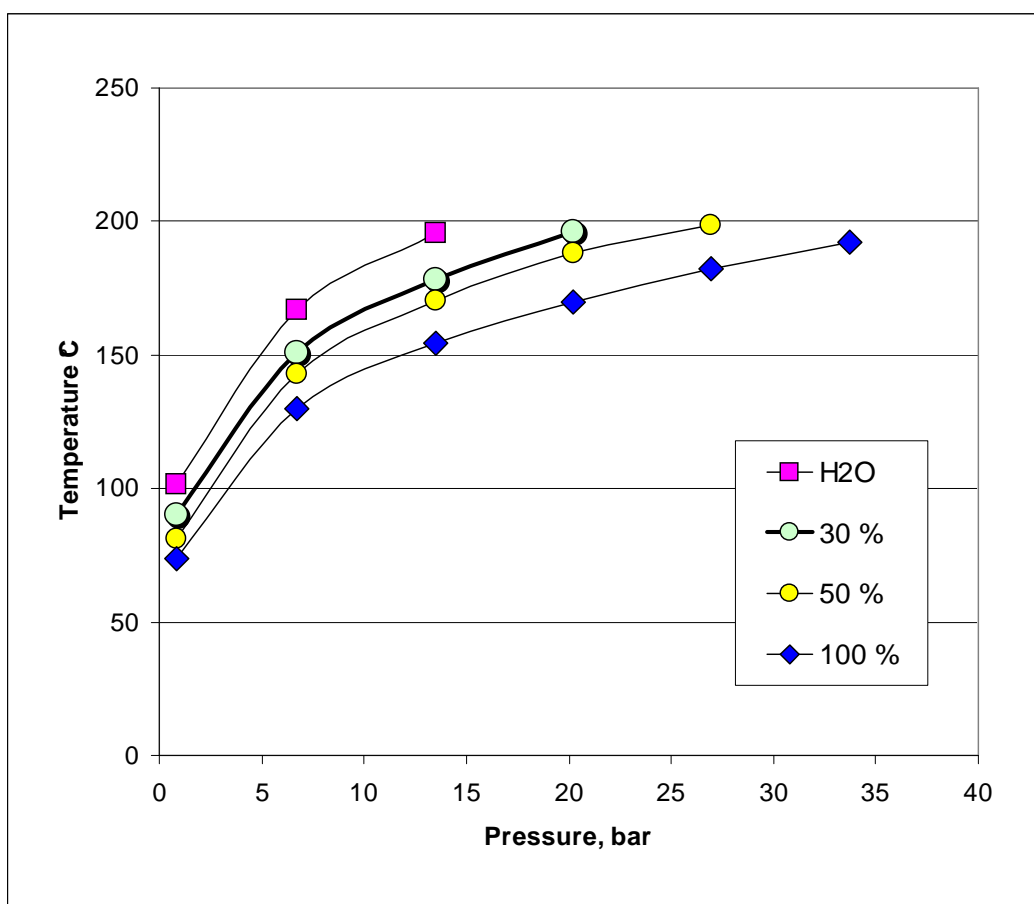
In the work of Malkov /22/ it was also shown that an increase in liquid viscosity decreases the speed of penetration of cooking liquor into wood chips. This phenomenon indicates that penetration of cooking liquors into wood will be hampered by the addition of alcohols to the impregnation liquor.



**Figure 31. Viscosity of water-ethanol mixtures at different temperatures /106/.**

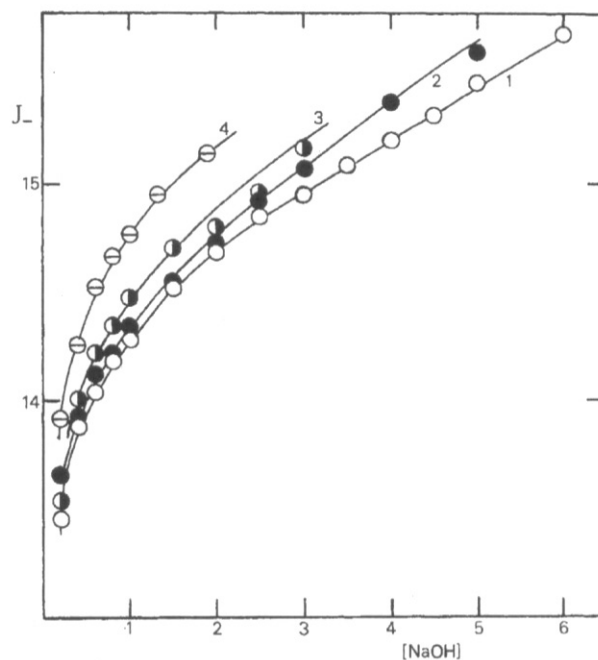
The solubility of inorganic chemicals is lower in solvents than in water. For instance, at room temperature, the solubility of NaOH in water is 1080 g/l whereas in pure methanol it is only 240 g/l /107/. This is the effect that Laroque and Maas used as the basis for their assumption of an “escaping tendency” of the inorganic chemicals towards the wood when adding alcohols in cooking.

Another characteristic that is affected is the steam pressure of the cooking liquor at elevated temperatures. This is particularly strong for lower alcohols. The vapor pressure of a 50 wt% methanol solution is 7.49 bar at 140°C, compared to 3.55 bar for pure water /106/. High pressure in the early part of the cook has been shown to have a positive impact on pulping uniformity /25/ due to increased penetration and this effect would counteract the impact of higher liquid viscosity to some extent. Adding organic solvents to an aqueous solution also has an impact on several other physical properties such as specific heat and thermal conductivity.



**Figure 32. Relationship between temperature and pressure for aqueous methanol solutions with various methanol concentrations /87/.**

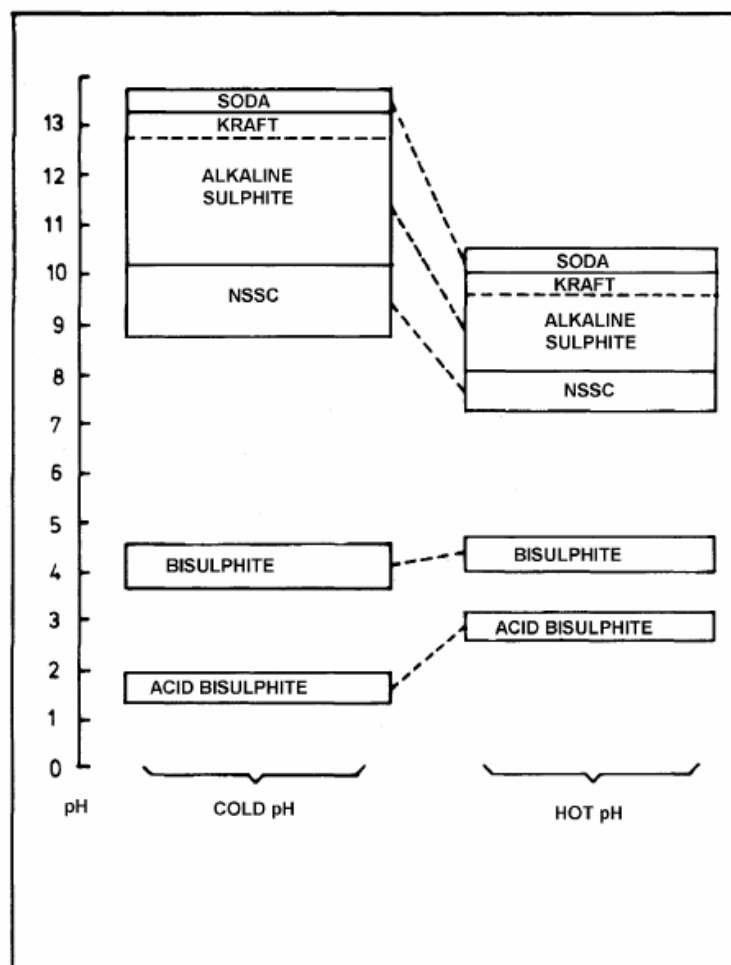
Apart from the easily measurable physical changes in cooking liquors, there are also changes in the physico-chemical behavior of the liquids. Figure 33 illustrates the basicity scale for the reaction which results in addition of hydroxyl ions ( $J_-$ ) as influenced by the addition of ethanol. Clearly, the value of  $J_-$  increases with increasing concentrations of ethanol. The increase is, however, not so big for the range of NaOH concentrations used in kraft pulping as for higher concentrations (concentrations in kraft pulping rarely go over 2 mol/l). At a constant NaOH concentration of 1.0 M the change in  $J_-$  when going from 1 to 50 vol % EtOH is from 14.28 to 14.48 (1.4%). Other researchers /108/ have shown that the proton availability (acidity) of hydrochloric acid in water decreases with the addition of alcohols. This also indicates that the addition of alcohols increases the basic component of an aqueous solution. In addition, the ionic product of water increases as methanol is added /109/.



**Figure 33. Dependence of the J acidity function on sodium hydroxide concentration in water-ethanol mixtures of different compositions: curve 1, 1%vol % EtOH; curve 2, 10 vol % EtOH; curve 3, 50 % vol EtOH; curve 4, 90 % vol EtOH /110/.**

Kiryushina et al. /111/, using lignin model compounds, have shown that the acid-base properties of lignin and reagents change with the addition of organic solvents such as methanol. They also claim that the reactivity of hydroxide anions increases, resulting in a high rate of cleavage of all C-O-C bonds in wood components. Their research indicates that a 1:1 volume ratio of water and methanol is the most efficient for lignin cleavage.

A possible way to interpret the effect of changing acid-base properties can be seen in Figure 34, showing the influence of temperature on pulping liquor pH. As can be seen, the effective pH of kraft pulping liquors drops considerably when going to the high temperatures used in pulping. If this effect is in some way changed by the addition of solvents, it is clear that it will have an impact on pulping speed. However, it would seem logical that the same effect would also have an impact on the yield of cellulose and hemicellulose. Such an effect is not seen in the literature that reports increased carbohydrate yield for processes with solvents.



**Figure 34. Cold and hot pH values for different cooking liquors /5/.**

A further interesting effect of small molecular solvents on other materials is that they lower the glass transition temperature,  $T_g$ , of polymers that come in contact with the solvent vapor /112, 113/. This effect is in principle due to the fact that the degree of structural order of the glassy polymer is reduced by the solvent entering the structure. This actually increases the speed of diffusion in the polymer. Wood behaves like a glassy polymer /30/, especially the hemicellulose part becomes very soft at elevated temperature. This makes for an interesting dilemma: on the one hand, organic solvents lower the speed of diffusion in the liquor phase and probably also in the entrapped liquor in wood; on the other hand, the same solvent might penetrate between the polymer chains in the wood structures and swell it up, thus making diffusion faster. It is possible that this effect also makes it possible for the hydrophobic lignin to come into contact with the hydroxide ions, carried in this case by the organic solvent.

During the work on the experimental side, the benefits of using alcohol in cooking were also found to manifest themselves when the alcohol is present only as a heating vapor. Aspects of this observation have been studied by Kovasin in calculations into heating efficiency and mass transfer /114/. The calculations show two very interesting aspects. Firstly, the density of methanol vapor is much higher than that of water steam at the pressure of saturated steam at typical pulping temperatures. This in turn means that the heat transfer capacity per unit volume of vapor is higher for methanol. Secondly, if the chips have first been impregnated with an aqueous solution and are subsequently heated

with methanol steam, there will be diffusion of methanol into the chip and water out. This might have interesting effects on the chemical activity of the inorganic ions in the cooking liquor. Exactly what those effects could be and how big they are is not clear.

#### **2.4.6 Conclusions from the literature survey**

As the name implies, an intensified process should be fast. Process speed has not received very much attention in pulping research during the past decades. Instead, the research has focused on pulp quality and yield. The biggest achievements in pulping research have been in understanding the impacts of front end changes on the runnability of the pulping process. However, the impacts of these parameters on overall pulping speed are not very big and it clearly has not been a priority to shorten the pulping time on this basis.

In contemporary research on the actual cooking stage, different researchers have tended to use radically different experimental set-ups, which makes it very hard to compare results in an unbiased manner. Also, the research has mostly been concerned with minor changes in parameters within the very restricted range currently used in industrial plants. This has not been a fruitful means for discovering radically new ways of producing chemical pulp. The problem with the incoherence of research methods is especially acute in the research into pulping additives such as alcohols.

As far as real intensified processes are concerned, the most promising research concerns steam phase pulping, high temperature pulping and the use of alcohols as process accelerants. Processes with increased concentration in impregnation, such as the WLI process, involve characteristics related to process intensification, such as attempts at ensuring as uniform reaction circumstances as possible for all parts of the wood. However, the benefits of these improvements have not been exploited in the form of increased process speed, so these processes can not be considered “intensified”.

Based on previous research, it is clear that there are certain techniques that can be used to intensify kraft pulping. The following techniques are presented as methods having an impact on the efficiency of kraft pulping:

1. Air removal prior to impregnation. Thorough steaming makes it possible to achieve complete impregnation of the wood chips. The effect of penetration on pulping speed is not big, but insufficient penetration will lead to formation of rejects and non-uniform pulping. Sufficient air removal is therefore a pre-requisite.
2. Impregnation concentration. A high impregnation concentration ensures transfer of sufficient chemicals to achieve fast delignification. This has the added benefit of reducing rejects from the pulping stage. This draws on the principle of ensuring as uniform processing of all molecules as possible.
3. Organic solvents have an accelerating effect on alkaline pulping. Some research also suggests improved yield. The underlying mechanism is unclear, but the effect is undisputable.
4. High temperature increases the speed of delignification. The pre-requisite of providing sufficient chemicals at the reaction sites has to be filled first.

Intensification methods 2 and 4 go against contemporary wisdom in pulping. The use of strong impregnation is in strong disagreement with so-called alkali profiling. However,

the results from steam phase pulping and WLI pulping experiments indicate that there is no adverse impact on pulp yield from using a steep alkali profile. The results from high temperature pulping contradict the theory that the differences in activation energies for delignification and carbohydrate cleavage indicate that low temperature pulping ensures improved carbohydrate yield. There is a clear contradiction in the literature on these points.

It is clear that there is a need for research into the actual impact on kraft pulping speed and yield of the intensification methods identified here. It is equally clear that a process taking advantage of the principles mentioned above may perhaps not be viable due to reasons of energy efficiency or the need for make-up chemicals. Still, the contradictions in the literature must be clarified before a process can be judged on these criteria.

## ***2.5 A critical review of methods used in kraft pulping research***

When attempting to study intensified methods of kraft pulping it is important to assure that the laboratory equipment used is flexible enough to allow testing the methods proposed. For example, if a short overall process time is aimed for, all sub-processes should be as fast as possible. In standard laboratory equipment the heating up of the digester vessel to reaction temperature often takes a disproportionately long time, something that is unacceptable when studying intensified processes.

An important part of any research is the use of laboratory experiments. In kraft pulping the importance of good experiments is accentuated by the fact that the unit size of the industrial equipment is so big that controlled experiments in a mill setting are impractical. Laboratory experiments are clearly needed, the question is merely how to perform the experiments so that they accurately describe the underlying phenomenon taking place. In an ideal situation, these trials should reflect the inner workings of the industrial equipment or the basic physico-chemical phenomenon in a clear and unambiguous way. This, however, is often far from the case, due to the fact that there are always several things happening at once (simultaneous mass transfer and reactions). Especially continuous digesters with their rapid heat-up and complicated chip bed properties are notoriously hard to simulate in the laboratory. Very little information has been published on the impact of laboratory pulping equipment on the process result. The available literature generally only describes the setup for a given experiment; comparisons are very seldom made with several types of equipment. Any difference in results compared to other research is then explained simply as a difference in the raw material. Only one study was found that compared a vertical stationary digester (forced circulation), an oil bath rotating autoclave and a digester with preheated liquor and reactor (a crude displacement digester)/115/. The following is a short review of typical experimental equipment and the kind of results obtainable with them.

Typical laboratory digesters are: air heated autoclave digesters, oil bath autoclaves, forced circulation digesters, flow-through digesters and displacement digesters

### **2.5.1 Air heated autoclave digesters**

The most basic way to perform pulping experiments is by using air heated autoclave digesters. In this type of reactor an autoclave, generally made of steel, is filled with chips and cooking liquor and heated in what is essentially a big oven. These reactors were quite



good in mimicking the conditions inside early tumbling batch digesters, but for today's processes they only give basic information about e.g. the suitability of a particular raw material for pulp production.

The biggest drawback with this type of equipment is its slow heat-up, meaning that all gradients disappear before reactions start. Also there is no possibility for sampling during the process. It is naturally possible to terminate a series of autoclaves at varying times, but the slow cooling down also makes this method of sampling unreliable. Also, the temperatures in the autoclaves can vary if the air flow is uneven; this is especially serious if only one autoclave is equipped with a temperature sensor /116/.

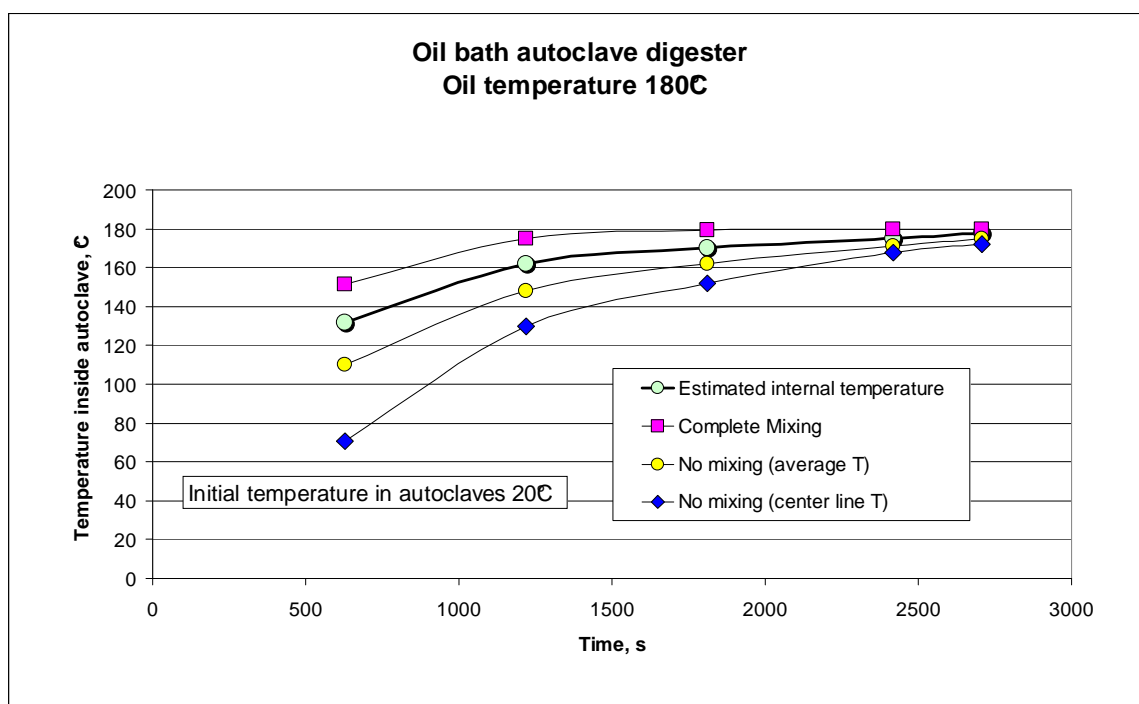
When using autoclaves without liquor circulation or addition it is clear that the concentration of both cooking chemicals and unreacted material is constantly decreasing. This leads to very slow reactions towards the end of the process.

### **2.5.2 Oil bath autoclaves**

By using pre-heated oil baths the heat-up of the autoclaves can be hastened and temperature variations within a batch of autoclaves virtually eliminated. Some versions of oil bath digesters even enable sampling of the cooking liquor during the pulping.

Even though the heat-up times are much shorter than with air heated digesters, the heat-up is far from instantaneous. Also, the cooling is as slow as for air bath digesters, leading to unnecessary changes in liquor and pulp composition. Autoclave pulping in general does not reflect industrial operations other than possibly the rotating digesters used for straw pulping in some very old mills. The heating and cooling of autoclaves in oil baths is in fact a lot slower than one might think. Calculations /117/ taking into account the heat-transfer coefficients of oil to autoclave and autoclave to liquor in the autoclave have shown that even in the event of total mixing inside the autoclave, a small autoclave (375 ml) reaches an internal temperature of 160°C only after 10 minutes, even if the oil is kept at 190°C. This can be regarded as an absolute minimum heating time.

According to Thode et al. /115/ the removal of carbohydrates at a given level of delignification is higher in tumbling oil heated autoclaves than in forced circulation or displacement digesters. This can probably be explained by stronger mixing in the tumbling autoclaves.



**Figure 35. Temperature inside steel cooking autoclaves when heated in 180°C oil bath. Series “Estimated temperature” represents best guess scenario, other series represent different assumptions regarding autoclave internal mixing.**

The calculations behind Figure 35 can be found in Appendix 1 of this thesis.

### 2.5.3 Forced circulation digesters

Forced circulation batch digesters were introduced in order to produce larger quantities of pulp in a way that more closely mimics industrial operations. These are vertical reactors with the chips in a basket through which the cooking liquor is led. The cooking liquor is circulated outside the digester and heated in a (generally) steam heated heat exchanger. These reactors give more control over the heating profile of the cook and also reflect the way simple batch type commercial digesters work. Some basic information can be found in work by Thode et al. /115/. Modern displacement heated batch digesters typically can not be simulated.

The heat up is still rather slow due to the large amount of steel that has to be heated, and the liquor-to-wood ratio can rise quite high compared to industrial applications. The speed of heat-up is set by the efficiency of the heat exchangers that generally are not designed to correspond to industrial processes. The use of forced circulation digesters has the advantage that it allows chip steaming prior to impregnation.

### 2.5.4 Flow-through digesters

In order to understand the kinetics of chemical reactions, information is needed about the speed of reactions at a certain concentration of reagents. In batch autoclave pulping the concentration of both alkali in the solution and lignin in wood decrease as long as the cook is in progress. To avoid this, in so called flow through digesters a large reserve of liquor is used in the digester and then circulated through the chip bed. In this way, the

concentration of the cooking liquor can be kept more or less constant throughout the experiment, though the concentration of unreacted material will naturally decrease as the experiment progresses. This method does a better job of simulating continuous digesters than conventional autoclave digesters, as it is possible to perform some alkali profiling.

The problem with this type of setup is that it does not resemble any industrial process. Therefore, care has to be taken not to misinterpret the results. For instance the washing out of organic components from the wood will be much more efficient in this system than it would in an industrial digester, especially if the cooking solution is based on pure water. When it comes to conclusions about kinetics of the reactions, one must remember that although the concentration of the surrounding liquor can be held constant, this does not necessarily say anything about the concentration at the reaction sites. And in the end, that concentration is what matters.

### **2.5.5 Displacement digesters**

The introduction of displacement heated batch digesters in the early 1990's brought a need to simulate this new process in the laboratory. To achieve this, a new generation of laboratory digesters was designed to make it possible to simulate the many liquor changes and displacements that take place in industrial digesters /118/.

Calculating alkali balances and other factors is difficult also with this type of digester, because displacement efficiency is not 100% ideal as some liquor might flow along the digester edges. The basic problem is that the digester is less than 1% of the size of a commercial digester, but the size of the wood chips is still more or less the same. This is a problem shared by all laboratory digesters, which has to be circumvented by acquiring a deep understanding of the phenomenon involved. However, good repeatability and much more realistic liquor-to-wood ratios and circulation speeds can be achieved with this type of digester.

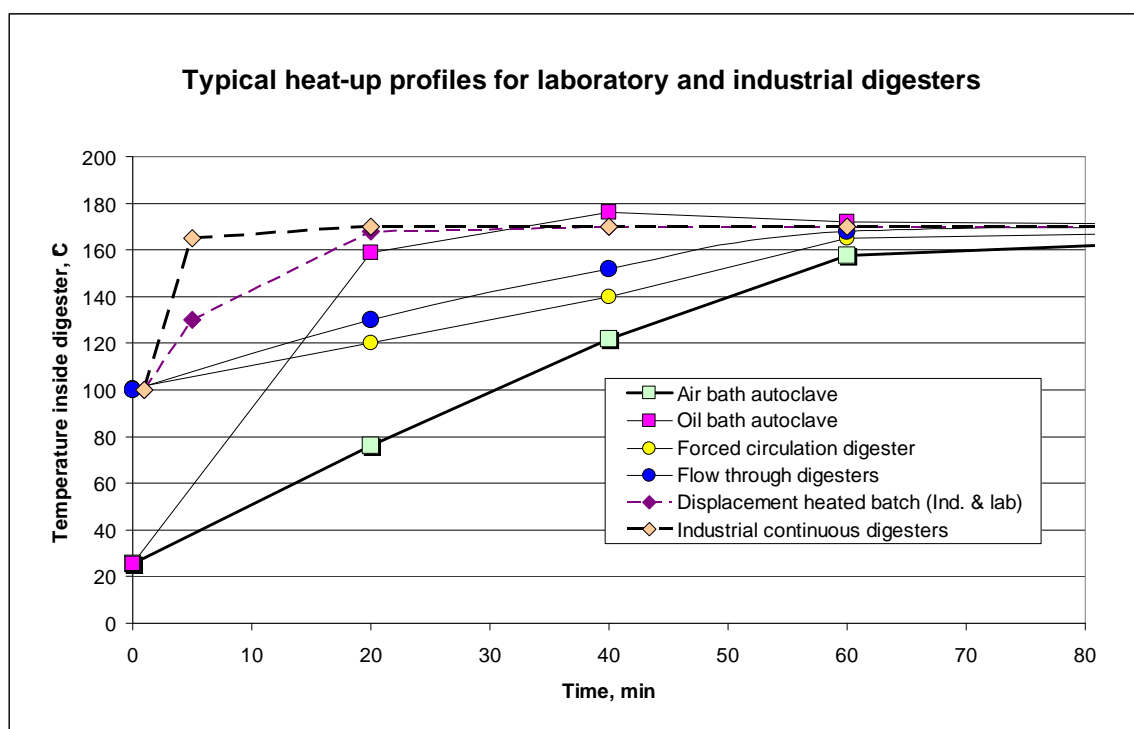
## 2.5.6 Laboratory vs. industrial pulping

In the following table, the different laboratory pulping methods are compared to the industrial processes currently in use.

**Table 4. Typical performance characteristics of industrial and laboratory scale pulping systems /5, 118,115,116/.**

	Front-end treatment	Heat-up time	Alkali profile	Liquor exchange method	Charged liquor-to-wood ratio	Liquor movement relative to chips	Mixing during operation
<b>Industrial method</b>							
▪ Continuous	Steaming	<10 min	Adjustable	Displacement	3:1	Co- & countercurrent	Very slight
▪ Displacement batch	Packing steam	20 min.	Adjustable	Displacement	5:1	Flow past	Slight
<b>Laboratory method</b>							
▪ Air bath autoclave	Room temp. impr.	60 min.	Decreasing	Drain & fill	5:1	Turbulent mixing	High
▪ Oil bath autoclave	Room temp. impr.	10 min.	Decreasing	Drain & fill	5:1	Turbulent mixing	High
▪ Flow through	Steaming possible	<10 min	Adjustable	Displacement	30:1	Flow past	High
▪ Forced circulation	Steaming possible	60 min.	Decreasing	Drain & fill	10:1	Flow past	High
▪ Displaced jacket heated	Steaming possible	15-20 min.	Adjustable	Displacement	5:1	Flow past	Adjustable

Table 4 is an attempt to group different industrial and laboratory pulping methods according to their performance characteristics. Such a comparison can never be completely accurate, as there are always variations between individual set-ups, but it is meant as a guide for further discussion. The table clearly shows that displaced jacket heaters can mimic industrial displacement batch pulping rather well, but no laboratory equipment is able to simulate completely all aspects of continuous pulping. Typical heat-up curves for different types of digester are presented in Figure 36.



**Figure 36. Typical heat-up profiles for laboratory and industrial digesters. Autoclave cooking typically starts at room temperature as there is no pre-steaming. In other cooking methods, the chips are generally heated to approximately 100°C by pre-steaming of chips.**

Figure 36 illustrates the problem in pulping research. The most commonly used equipment falls short of accurately mimicking the conditions in industrial digesters. Only displacement heated batch digesters can be accurately simulated in the laboratory by more advanced laboratory digesters. There is no equipment currently available that would be able to simulate industrial continuous pulping.

Due to the use of laboratory equipment with slow heat-up, the experiments will fail to show the mass-transfer limitation and alkali depletion that can happen when using fast heat-up. As a results, the results become unrealistic. In a study into the fastest possible way of producing kraft pulp, where all sub-process should be as fast as possible, such restrictions are unacceptable.

### 3 Experimental

The findings of the literature review support the original starting hypothesis, i.e. that there is room for process intensification in kraft pulping by improving mass-transfer, using high temperatures and by applying organic solvents. However, as process speed has not been a key issue in research conducted so far, the literature is fragmented and gives few absolute answers. This allows plenty of scope for new research and new knowledge, but only if fast heating processes can be carried out at laboratory scale. Therefore, the first step in the present experimental research was designing, building and commissioning of a new kind of laboratory cooking equipment, which would solve the obstacles of fast heating. The new “PuPu” digester, nick-named according to its push-pull working principle, was the only type of cooking equipment in the present study that made it possible to apply a unique range of heating and cooking conditions, while avoiding the fundamental difficulties arising from the use of multiple equipment with individual heat and mass transfer properties.

To obtain the data needed to test the starting hypothesis and to draw relevant conclusions on process intensification, the following experimental entities were carried out:

- kraft cooking experiments in liquid phase with varying impregnation and heating-up
- kraft cooking experiments in water steam phase
- kraft cooking in the presence of methanol
  - o varying impregnation and heating-up time
  - o varying methanol allocation
  - o minimizing methanol amount and applying methanol vapor phase cooking
  - o varying impregnation concentration and alkali-to-cook
  - o varying cooking temperature
  - o varying chip thickness

In addition to the series of cooking experiments, a number of complementary experiments were carried out. These included impregnation experiments measuring penetration, the effect of pressure in cooking, and replacing methanol by other solvents.

#### **3.1 Push-pull (“PuPu”) cooking equipment**

As discussed in chapter 2.5, the development of industrial kraft cooking equipment has been quite rapid, resulting in various widely used fast heating operations, such as steam-phase digester top and hot cooking liquor displacements. In contrast, most laboratory cooking research has been and still is being carried out with unrealistic equipment, resulting in a slow heating rate or an uncontrolled and very non-linear heating rate in autoclave-oil bath systems. In the present research challenge, small size and very fast heating were key requirements, which none of the existing techniques fulfilled.

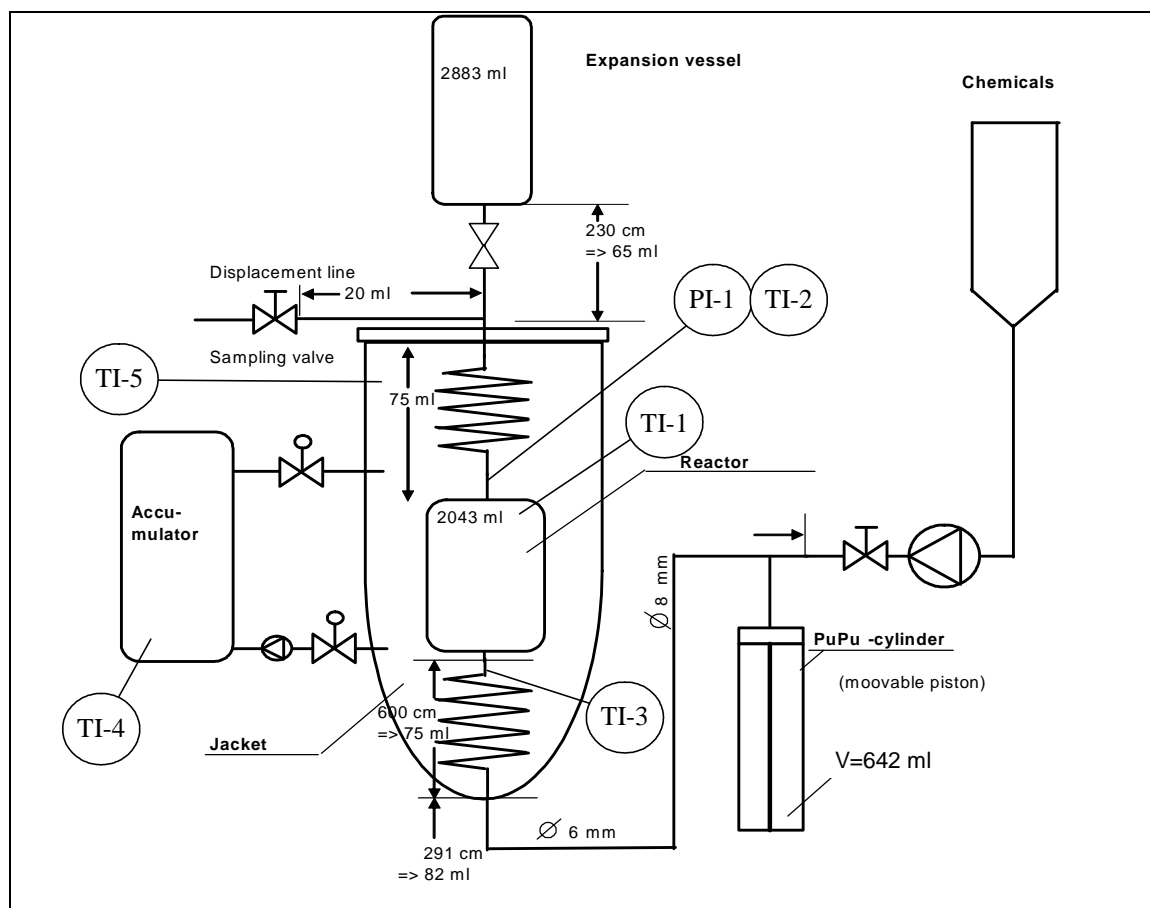
##### **3.1.1 Working principle**

After investigating the heating dynamics of autoclaves, it became evident that mixing and moving the liquor in an autoclave positioned in a hot water jacket would improve heat

transfer a lot. It would also eliminate the slow-down of the rate of temperature change at lower  $\Delta T$ , because of its stationary chip-liquid bed system. As mixing of the chip-filled autoclave is impossible at reasonable liquor-to-wood ratios, the only way to improve mixing is to move the chip bed liquid in and out to heat exchanger coils positioned within the same hot water jacket as the autoclave. The push-pull motion of the liquid is provided by a piston in the cylinder outside of the hot equipment heart. The liquid movement is propagated hydraulically and the movement space at the other end of the system is a gas space working as a gas spring, pushing back the liquid towards the autoclave and the back-stroke of the piston in the cylinder.

The main parts of the PuPu cooking equipment are illustrated in Figure 37. The heart of the system is a digester vessel surrounded by a water jacket. Both the inlets and outlets of the digester vessel are in the form of coiled pipes that pass through the water jacket. This ensures that heat transfer is very fast and that the liquor entering the digester is at the desired temperature. The temperature of the water jacket can be changed very rapidly by either bringing in hot water from the hot water accumulator or by using cold tap water.

Efficient heat transfer is generated by a movable piston in a cylinder connected to the liquor system. The piston can be used to move liquid from the digester back and forth through the system including the heat-exchange coils, causing very efficient heat transfer into the vessel. The mixing within the digester will be quite efficient as a consequence of the moving liquid, something that has to be taken into account when considering mass transfer aspects in a possible scale-up of the process results. A typical heat-up time from 80°C to 170°C is as short as 3 minutes, compared to more than ten times as much for conventional systems.

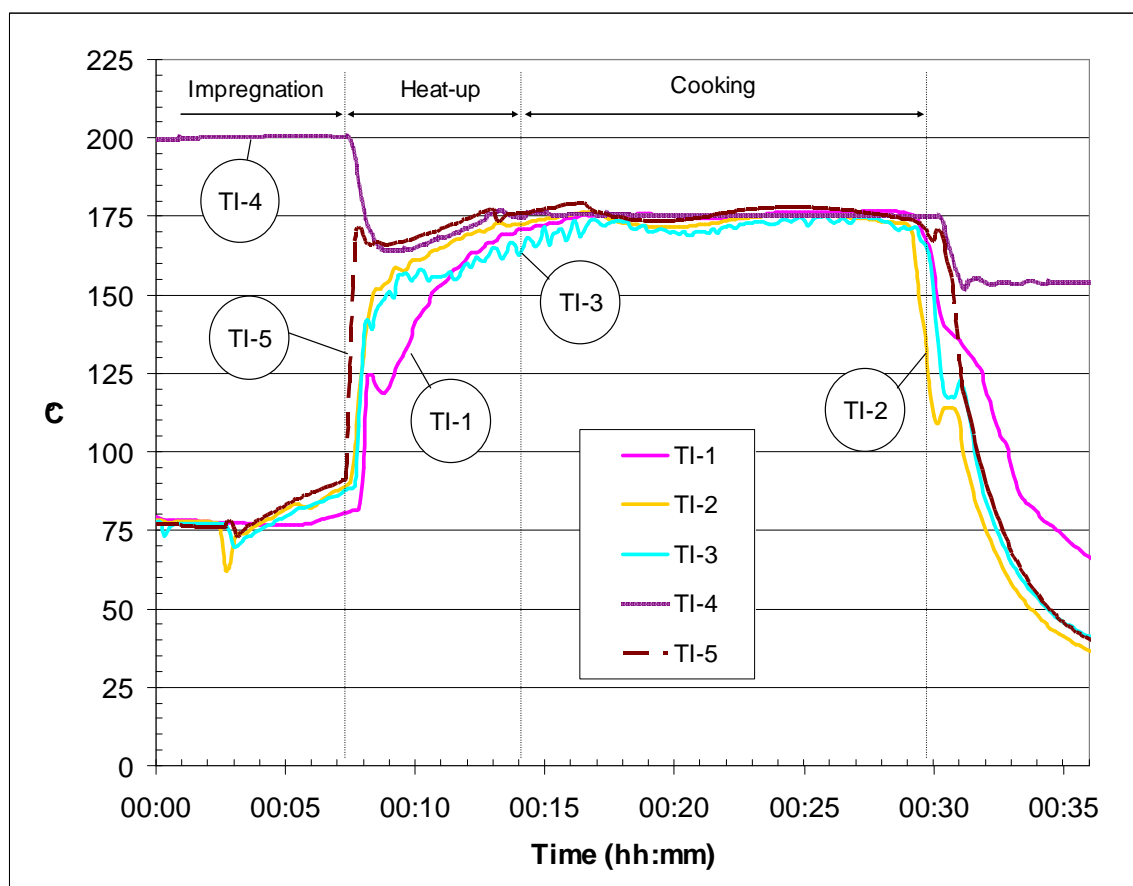


**Figure 37. Push-pull digester (not in scale). Internal pipe volumes indicated.**

The digester system is also equipped with a sampling valve with cooling that enables liquor samples to be drawn during the cook. However, this method of sampling can not be used in vapor phase pulping, as the liquid level is below the outlet of the sampling line.

The graph in Figure 38 shows typical process parameters for a methanol vapor phase cook using the push-pull digester. The jagged line depicting the temperature of the entering liquor is due to the action of the piston. The numbering of the lines is as indicated in Figure 37.





**Figure 38. Typical temperature and curves for the end of the impregnation stage, the heat-up and cooking stages of a cooking experiment using the push-pull digester. 175°C cook to 400 H-factor, 7 minutes heat-up. Positions of temperature indicators as in Figure 37**

### 3.1.2 Liquor-to-wood ratio

The short heat-up time achieved with the PuPu digester is to a large extent achieved by the rapid movement of the liquid as it is pumped back and forth using the push-pull cylinder. The moving liquid passes through the heat-exchange coil at both ends of the digester, leading to very efficient heating of the liquid. As the push-pull cylinder is moved down, cooking liquor is withdrawn from the digester vessel to fill the pumping cylinder. This means that the amount of liquor in contact with wood, or in other words the effective liquor-to-wood ratio in the digester, is changing. In the text, two different liquor-to-wood ratios will be used: the theoretical and the effective L:W. The theoretical L:W is calculated based on the total amount of liquid charged to the system and the moisture present in the wood. This includes the liquid that will end up filling pipes etc. in the system. The effective L:W is the amount of liquid in contact with the chips in the digester. A maximum and a minimum value will be given for this, based on how much liquid is flowing in and out of the digester (pipes outside the digester vessel have an actual volume of 157ml, the push-pull cylinder 642ml, typical pumping frequency 1/min). The reason why it is considered important to make a distinction between the amount of liquor in the system and the amount in direct contact with the wood is that the mixing behavior inside the digester is not known in detail. Also, the whole concept of vapor phase pulping is slightly diffuse, as there will always be condensation of vapor on the

chips leading to liquid being present. This underscores the importance of knowing what is inside the digester at all times so that the real reaction conditions can be known.

### **3.2 Push-Pull (PuPu) cooking methods**

In the course of the investigations, several test series with different setups were performed. The variations included trials with different chip dimensions, different cooking chemicals and different liquor circulation schemes. To explain every detail of every variation in the setup would be impossible, so the following is a discussion of the main pulping methods used, and how these compare to each other. Complete listings of the experimental conditions and pulping results can be found in the appendixes.

In view of the possibility to change all pulping parameters over a very wide range, the question was how to ensure fair comparison between the cooking results. The method employed in the current research was to lock the end-of-cook alkalinity at a realistic level of 5-10 g/l EA as NaOH. In industrial systems a clear positive alkalinity is needed to make evaporation and firing of black liquor possible. By doing this it was ensured that there was still some delignifying power left in the liquor, and still the amount of alkali in the cooks was not completely unrealistic. In the course of the research, many experiments led to cooks where the alkali was consumed before the end of the cook or where there was a surplus of alkali (higher than 10 g/l). Such results have been left out from the current discussion, unless explicitly acknowledged in the text.

All push-pull reactor cooks, except those performed with geometrical chips, were performed with fresh chips corresponding to 400 g O.D. wood. Fresh wood was used in order to ensure the greatest possible relevance of the results to a real world situation.

The following general experimental setups were performed:

- Conventional batch pulping
- Displacement heating
- Vapor phase cooking

The main part of the research was performed with cooking at 175°C. This temperature was chosen as one that can be easily reached using medium-pressure steam (12 bar) in a mill situation. The H-factor was used to describe the time-temperature sum in the experiments, as is common practice in the industry.

#### **3.2.1 Steaming**

In all pulping experiments the chips were steamed prior to pulping. The steaming was performed by passing steam through the chip bed in the digester while maintaining digester pressure at 1.2 bars. The steaming was continued until there was steam coming out from the digester system, i.e. the chips were heated so much that the steam no longer condensed. The water jacket was held at 95°C during steaming. After steaming, a mild flow of N<sub>2</sub> gas was briefly led through the system in order to flush out steam condensate from the reactor and piping. Condensate was removed to eliminate any inaccuracies in the liquor balance calculations.

### 3.2.2 Conventional batch pulping and methanol impregnation cooks

To obtain a relevant reference, batch kraft pulping was performed using the same chips and the same digester. All process variations were compared to this reference, and for any variation to be considered an intensification, this is the level of pulping speed that it must surpass.

When performing conventional pulping experiments, the delignification chemicals were introduced into the digester after the steaming so that the chips were completely submerged and part of the liquor was in the expansion vessel above the digester. The system was left like this for the duration of the impregnation period. When heat-up started, the push-pull piston was operated to ensure quick and uniform heat-up. The cook was kept at temperature until the H-factor target had been achieved. When the cook was ready, the temperature of the water jacket was lowered to 90°C and the cook was stopped. Once cooled, the pulp was washed with 2 l of clean water before removal from the digester. The same procedure was used in the methanol impregnation cooks described later in the text, the difference being in the composition of the impregnation liquor. In the methanol impregnation cooks, 50% of the volume of the cooking liquor was replaced by methanol.

Impregnation liquor:	2000 ml
L:W <sub>Theoretical</sub> :	6.3:1
LW <sub>Real</sub> (min-max):	4.3:1-5.9:1
Impregnation temperature:	80°C
Impregnation time:	60 min
Impregnation pressure:	0.3-0.5 bar
Reaction temperature:	175°C
Heat up-time:	5-7 min

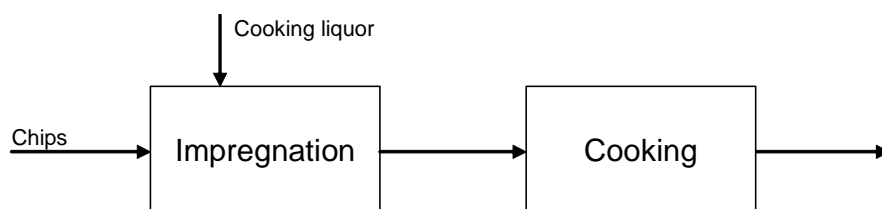


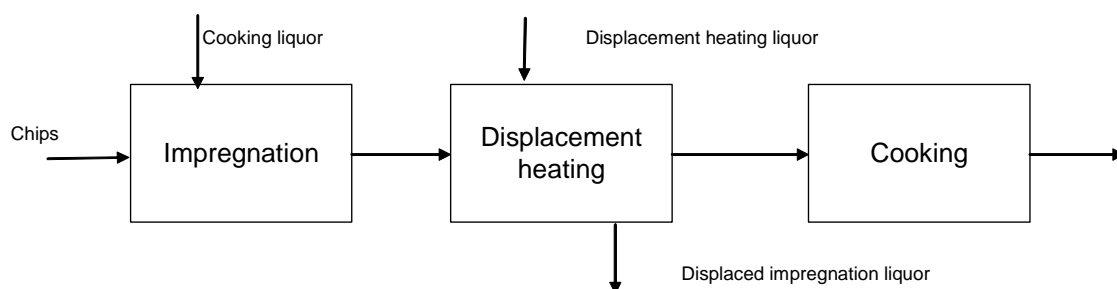
Figure 39. Schematic presentation of the process steps in conventional batch cooking.

### 3.2.3 Displacement heated cooks / MeOH cooking

A series of experiments was performed by first impregnating the wood with the cooking chemicals and subsequently displacing the impregnation liquor with either water or an organic solvent. Simultaneously with the displacing, heating was started. In this way, the displacing medium becomes the heating agent. The system was then agitated by means of the push-pull piston for the duration of the cooking time.

When the cook was completed, the temperature of the water jacket was lowered to 90°C and the cook was stopped. Once cooled, the pulp was washed with 2 l of clean water before removal from the digester.

Impregnation liquor:	1500 ml
L:W <sub>Theor.</sub> in impregnation:	5:1
LW <sub>Real</sub> in impregnation:	4.6:1
Impregnation temperature:	80°C
Impregnation time:	60 min
Impregnation pressure:	0.3-0.5 bar
Impregnation liquor removed:	800 ml
Heating liquor:	1200 ml (H <sub>2</sub> O or methanol)
L:W <sub>Theor.</sub> in pulping:	6:1
LW <sub>Real</sub> in pulping:	4:1-5.6:1
Reaction temperature:	175°C
Heat up-time:	5-7 min



**Figure 40. Schematic presentation of the process steps in displacement heated cooking.**

### 3.2.4 Vapor phase cooks

In the third main variant of pulping, the chips were first impregnated for 60 minutes. Then the digester was emptied of excess liquor before introducing a relatively small amount of the heating medium, while simultaneously turning up the system temperature. This leads to a situation where most of the chips are not submerged but only heated by the atmosphere of hot vapor surrounding them. The chips on the bottom of the digester will, however, come into contact with the heating liquid when the push-pull piston is in the top position. After the cook, 700 ml of clean water was added to the digester and left to diffuse for 1h at 50°C. This liquor was then withdrawn and sampled for end-of-cook alkalinity (the result is calculated based on the volume of liquid in the digester prior to filling with wash water). The reason for this procedure was quite simply that it would otherwise be impossible to get a sample of the liquid inside the digester, since the liquid level is below the sampling valve outlet.

Impregnation liquor:	1700 ml
L:W <sub>Theor.</sub> in impregnation:	5.6:1
LW <sub>Real</sub> in impregnation:	5.2:1
Impregnation temperature:	80°C
Impregnation time:	60 min
Impregnation pressure:	0.3-0.5 bar
Impregnation liquor removed:	1500 ml
Heating liquor:	600 ml (H <sub>2</sub> O or methanol)
L:W <sub>Theor.</sub> in pulping:	3.3:1
LW <sub>Real</sub> in pulping:	1.3:1-2.9:1
Reaction temperature:	175°C
Heat up-time:	5-7 min

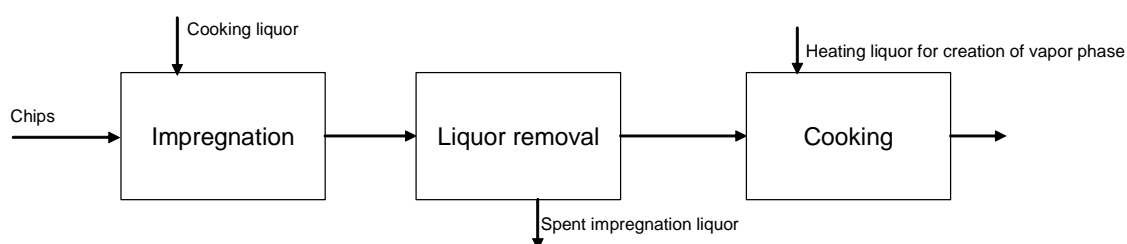


Figure 41. Schematic presentation of the process steps in vapor phase pulping

### 3.3 Testing after pulping

#### 3.3.1 Disintegration and screening

After pulping, all pulps were wet disintegrated for 2 minutes in a laboratory disintegrator using hot water and subsequently screened using a laboratory screen with 0.25 mm slots.

#### 3.3.2 Pulp analysis

Total yield, screened yield, rejects, kappa number, viscosity and brightness were determined for all pulps. Kappa number, viscosity and brightness was determined for the screened portion of the pulp.

In comparing the results, lignin yield was used. The lignin yield on wood was calculated based on kappa number and total yield, as explained in section 2.1 of the literature review.

### 3.4 Further testing methods

#### 3.4.1 Impregnation tests

Some basic tests were also performed using the impregnation apparatus described in Malkov's thesis /22/. Some of the handmade softwood chips used in that study had been kept refrigerated and were also used in the present study.

In the experiments, handmade geometrical pine heartwood chips were submerged in a wire basket attached to a balance. This made it possible to measure the penetration of liquor into the chips as a function of time. Tests were performed using chips with a size of 35x15x4 mm. Separate tests were made using pure water, a mixture of water and mill white liquor and a mixture of water, mill white liquor and methanol as the impregnating media. Tests with all liquors were performed using 1-, 5- and 9-bar overpressure at 25 and 70°C.

The same batch of chips was also used in the tests concerning the impact of digester pressure on kraft pulping, as is indicated in the results section dealing with those experiments.

### **3.4.2 Pulp uniformity testing**

Selected pulps were tested for delignification uniformity using single fiber kappa analysis and FT-IR measurements. The procedures are described elsewhere [119, 120]. The services were provided by the laboratories that have developed the processes. Their help is greatly appreciated.

## **3.5 Materials used**

### **3.5.1 Chips**

The softwood cooks were performed using softwood chips from the Botnia Rauma mill. The chips were collected in three different batches, so a slight variation in the spruce/pine ratio does exist between the raw materials over time.

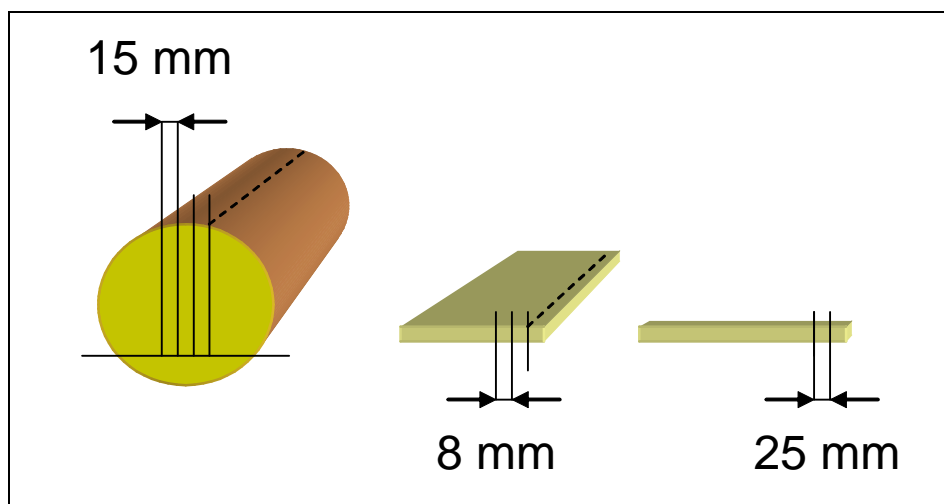
The tests with commercial chips were performed using 400g O.D. chips per cook. The dry matter content of softwood chips was around 43%. When packed into the digester using a wooden club, this left 1310 ml free space in the digester. In other words, the wet wood had a packing degree of 0.2 kg/dm<sup>3</sup> of digester volume.

### **3.5.2 Screening**

The chips were thickness screened on a vibrating screen using screens //8, //6, //4 and // 2 prior to pulping. The chips used were chosen to be >//2 and <// 6. The reason to use a rather narrow sample of thickness screened chips was to ensure uniformity in the rather small digester.

### **3.5.3 Geometrical chips**

In order to gain a deeper understanding of the mechanisms involved, a series of cooking experiments was conducted using geometrical softwood chips. The chips were produced by felling one pine tree in the Lohja area and cutting it into boards that were then cut into long slabs that were subsequently cut into chips. The chips measured 8x15x25 mm (thickness x width x length). Heartwood and sapwood were separated and pulped separately.



**Figure 42. Procedure for preparation of geometrical chips**

Due to the bigger size of the geometrical chips compared to the mill chips only 340 g as o.d. could be fed to the digester for each cook.

Similar chips were also used in the impregnation experiments and high pressure cooking. Those chips originated from Malkov's research and are described elsewhere /22/.

### **3.6 Chemicals**

Mill white liquor from the Botnia Rauma mill was used for the experiments. The sulfidity of the mill white liquor was 40%.

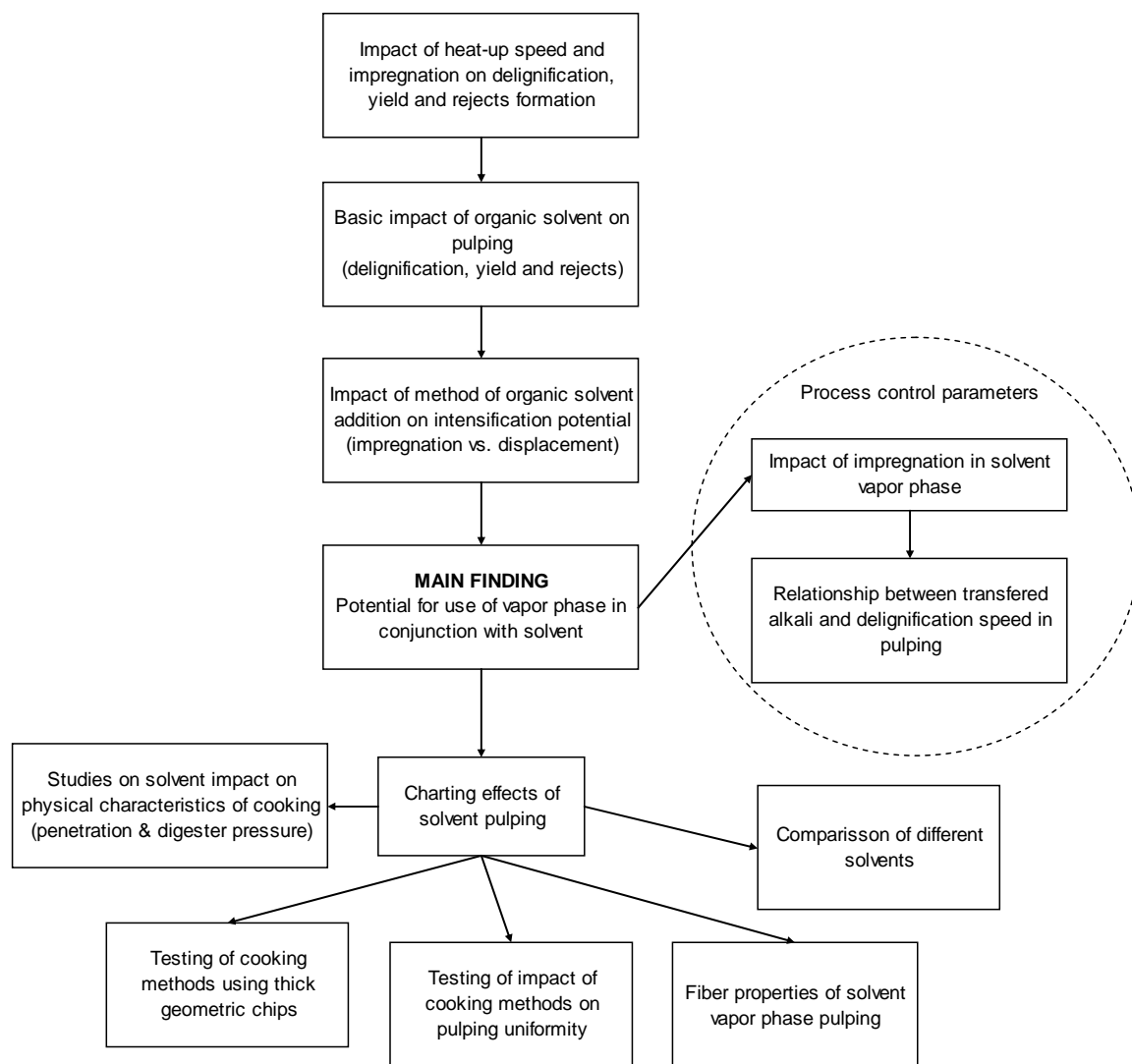
The alkalinity of the white liquor was determined according to the SCAN-N 2:63 standard. Spent impregnation liquors, generally having an EA of 40 g/l or over were titrated to pH 9.5 with the same chemical additions as in SCAN-N 2:63. This was done to ensure that the uptake during impregnation is correct (the EA in N2:63 is calculated based on titration using indicators with the inflection point at pH 9.5). For black liquors a variation of the Wilson method of titrating to pH 11 was used.

## 4 Results

Characteristic of the present research was its explorative nature: how best to intensify and speed up kraft cooking. The first part of the results deals with the question what the limits for kraft pulping are, and how much it can be intensified using only minor changes on parameters such as impregnation time and heat-up. After showing that heating-up can be very fast, emphasis is put on the required mass transfer conditions. By this means the kraft pulping barriers become understandable. The quest for intensification is then continued by various studies on the effect of methanol as an accelerator of kraft pulping. Experiments to minimize the methanol amount led to a new technique for intensification: cooking by methanol vapor. The rest of the cooking research was then focused on understanding the implications and uncovering optimal conditions. In addition to these main series of cooking experiments with the PuPu equipment, several completing results are given. Figure 43 illustrates a “family tree” of the research and results thereof.

The present work covers over 600 cooking experiments and more than three years of research work. The starting hypothesis took physical shape as the research depicted above and various experimental research lines evolved, ceased and continued. It was decided at the beginning that exploring new kraft and methanol-kraft pulping schemes would be the main target of the research, meaning, among other things, that it was not possible to use any single rigorous statistical design of experiments. Instead the main results and their confidence limits were analyzed by suitable statistical tests.





**Figure 43. Schematic presentation of the basic directions of research**

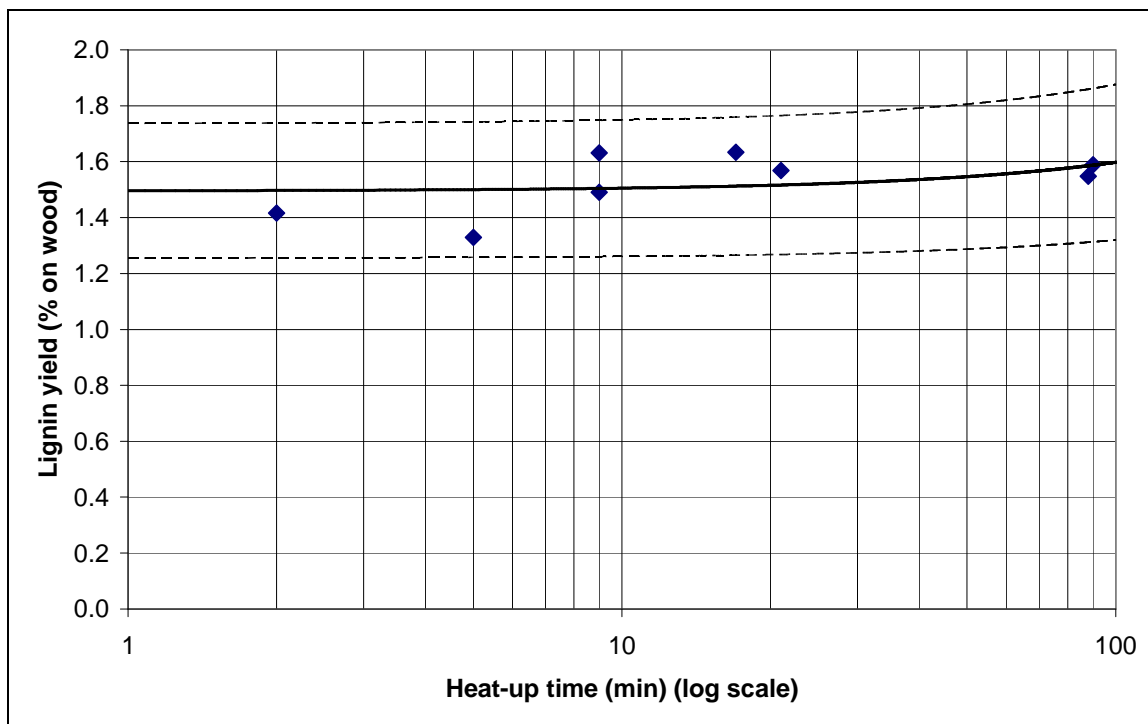
As is typical of research into complex matters, every new finding brought with it a new set of questions. As can be seen from Figure 43, the web of research soon started growing as the interesting findings started piling up. The following sections present the results of each group of experiments and the rationale behind subsequent experimental directions.

#### **4.1 Barriers of conventional batch pulping**

To find ways to improve the kraft pulping process, the basic correlations for the conventional kraft process had to be found. The first parameter to be studied was the impact of heat-up time on the pulping result. A series of cooks was performed with the same alkali charge and same cooking time as determined by the H-factor. The only parameter to be changed was the heat-up time that was changed between 2 and 90 minutes as seen in Table 5. The results are shown in Figure 44 and Figure 45.

**Table 5. Experimental parameters in experiments with different heat-up times.**

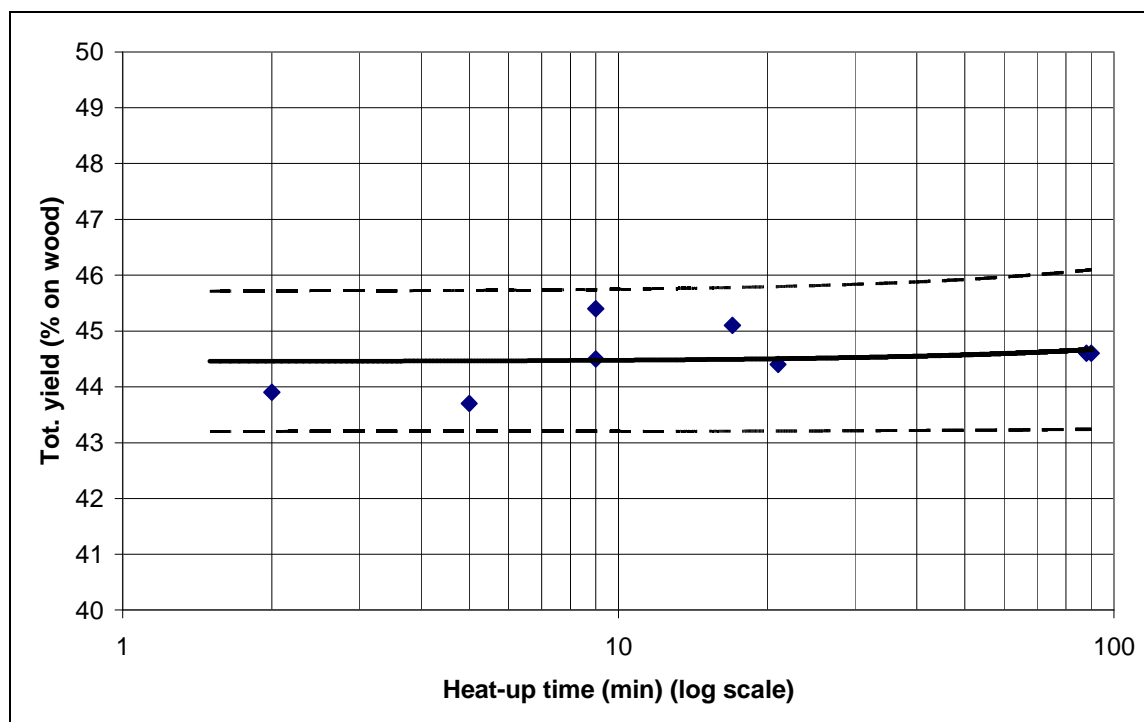
<b>Impregnation time (min.)</b>	<b>Heat-up time (min.)</b>	<b>H-factor</b>	<b>Alkali charge (% EA on wood)</b>
60	2-90	2300	25



**Figure 44. Lignin yield vs. heat-up time for batch kraft cooks. H-factor 2300, EA charge 25% on wood as NaOH. 60 minute impregnation at 95°C cooking temperature 175°C. Linear regression trend with 95% confidence intervals shown.**

Visual inspection of the data points fails to identify a clear trend. Linear regression gives the relationship between heat-up time and lignin yield as  $\text{lignin yield} = 0.001x(\text{heat-up time}) + 1.49$ . As the slope of the line is very close to zero it is clear that lignin yield cannot be estimated based on the heat-up time. Adding 95% confidence intervals for the regression further underscores the fact that delignification is independent of heat-up time. The apparent curvature of the trends in Figure 44 is due to the logarithmic scale used for the x-axis.

The same observation can be made for the yield results for the cooks as seen in Figure 45. No clear trend can be seen in the results, the variation is within the range of normal experimental accuracy. Linear correlation between heat-up time and total yield gives the equation  $\text{total yield} = 0.002x(\text{heat-up time}) + 44.5$ . Again, the slope is very close to zero pointing to independence of yield from heat-up time.



**Figure 45. Total yield vs. heat-up time for batch kraft cooks. H-factor 2300, EA charge 25% on wood as NaOH. 60 minute impregnation at 95°C cooking temperature 175°C. Linear regression trend with 95% confidence intervals shown.**

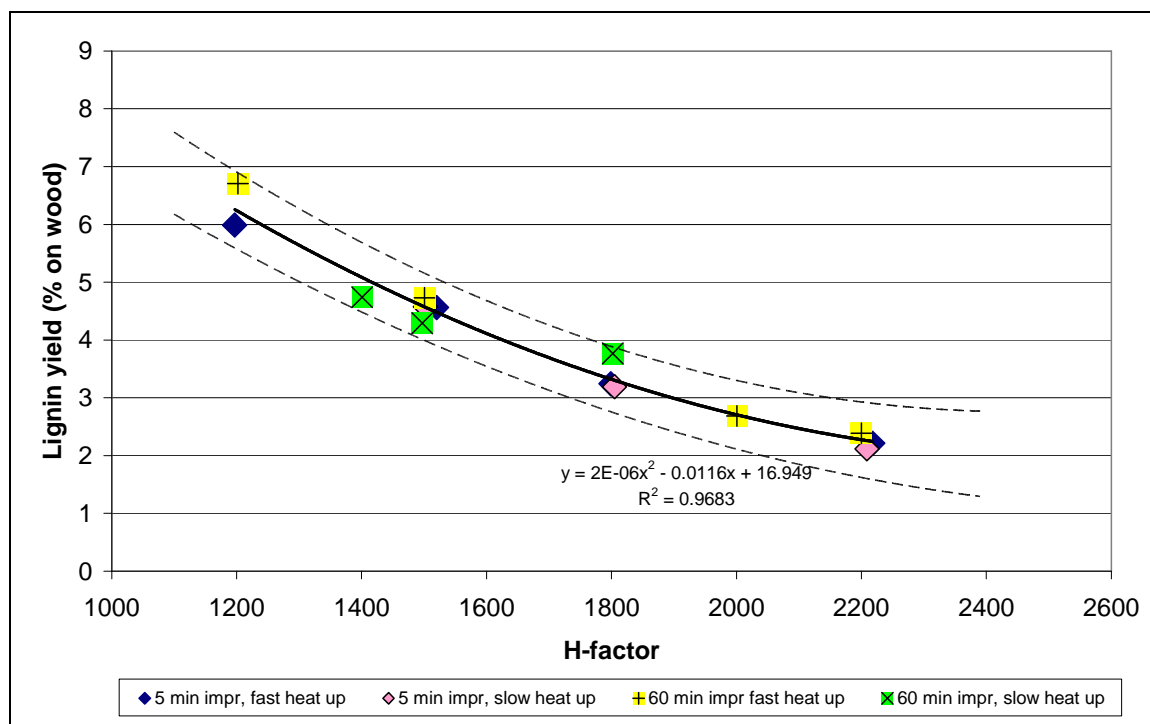
As is seen, changing the heat-up time has very little impact on the pulping results when impregnation has been thorough. In these first experiments the cooking time was so long that some of the possible variation can be masked by subsequent leveling out. The next step was to try to find combinations of impregnation and heat-up that would give the highest possible yield and fastest possible cook.

To study the combined effects of impregnation and heat-up, a series of experiments was conducted. In this series two levels of impregnation time and heat-up time were chosen: 5 and 60 minutes' impregnation and 5 and 90 minutes' heat-up time. Several experiments were performed with all combinations, using different H-factors and alkali charges so as to keep the end-of-cook alkalinity constant. The results are presented in the following figures.

**Table 6. Experimental conditions used in study on impregnation and heat-up**

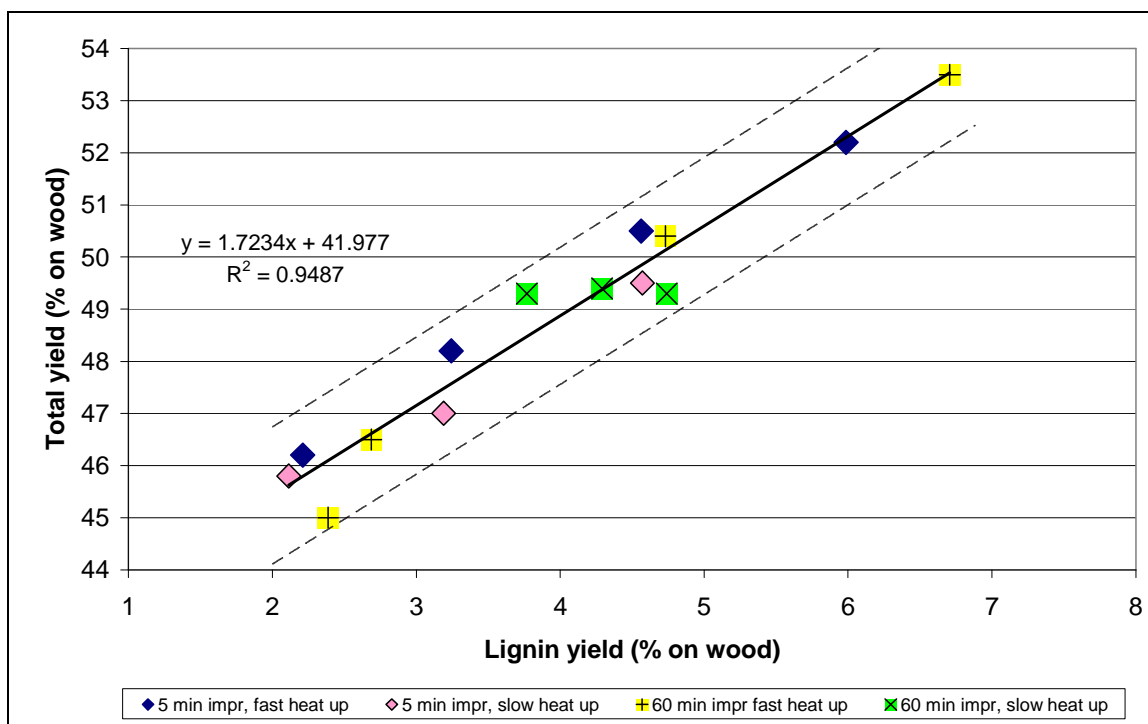
	Impregnation time (min.)	Heat-up time (min.)	H-factor	Alkali charge (% EA on wood)
1.	5	5	1400–2200	19.0-21.3
2.	5	90		
3.	60	5		
4.	60	90		

Four cooks were performed for both of the short heat-up combinations, whereas three were performed for the set-ups with longer heat-up. The impact on delignification speed is seen in Figure 46.



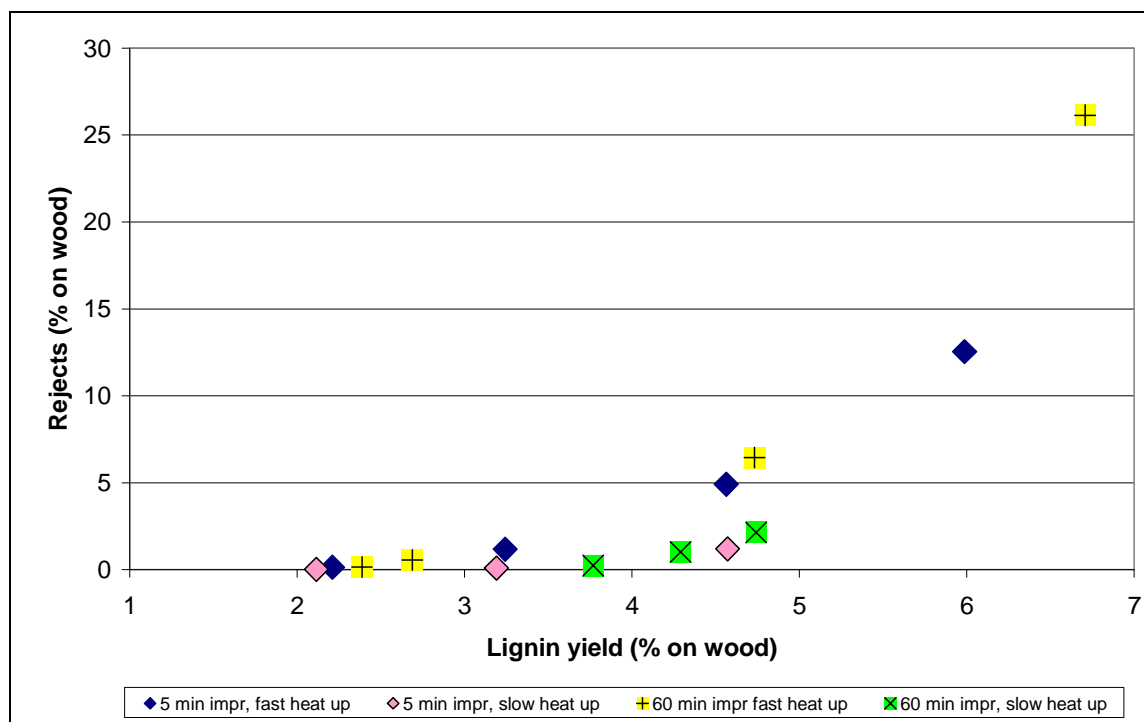
**Figure 46. Lignin yield. vs. H-factor for batch kraft cooks to constant EoC alkalinity using varying impregnation and heat-up procedures. 95% prediction band for regression model for individual values indicated with dashed lines.**

When looking at the distribution of points in Figure 46, it is hard to recognize any clear pattern based on impregnation and heat-up times. No matter how impregnation and heat-up were performed, the end result was more or less the same with regard to the degree of delignification. As shown in the figure, all the results can be predicted by a single regression model and all results fall within the 95% prediction band of this model.



**Figure 47. Total yield vs. lignin yield for batch kraft cooks to constant EoC alkalinity using varying impregnation and heat-up procedures. 95% prediction interval for individual values shown by dashed lines.**

In the same way as for lignin yield vs. H-factor in the previous figure, no clear trend can be seen for the total yield vs. delignification degree (lignin yield) presented in Figure 47. This is particularly apparent when looking at the cooks with 60 minutes' impregnation and slow heat-up, the total yield is virtually unchanged over a band of almost 2 percentage points of lignin yield. The points for cooks with short impregnation and fast heat-up are all above the linear trend, but the difference is so small as to be statistically insignificant.



**Figure 48. Rejects vs. lignin yield. for batch kraft cooks to constant EoC-alkalinity using varying impregnation and heat-up procedures.**

For the rejects at different degrees of delignification presented in Figure 48 it seems that slow heat-up is preferable when aiming for low rejects. This is understandable as more time is available for diffusion of chemicals within the chips. It is interesting to note that 60 minutes' impregnation is not sufficient to markedly change the situation; a short heat-up time always gives higher rejects at a high lignin content than a long heat-up.

The cooks yielded quite clear limits in cooking speed that seem to be hard to surpass with conventional pulping methods. The limit is basically set by the alkali charge, as the end-of-cook alkalinity is kept constant and the liquor-to-wood ratio has to be around 5 to submerge the chips. Together, the charge and the liquor to wood ratio constrain the concentrations that can be used to a rather narrow band. From the point of view of intensification, it is seen that impregnation and heat-up can be kept short for well-steamed chips, as long as rejects can be kept low by pulping to a low enough lignin yield.

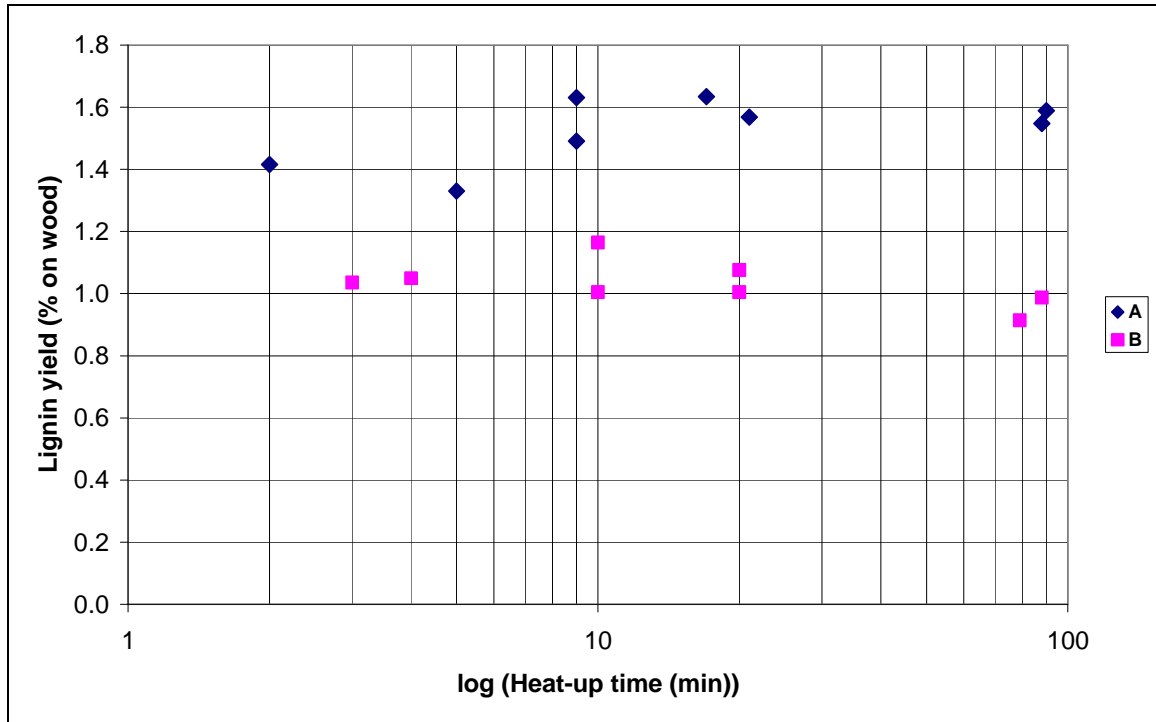
## **4.2 Benefit of using methanol in kraft pulping**

As seen in the literature review, several researchers have found addition of methanol to have a positive impact on delignification. Earlier unpublished work indicated that fast heat-up enhances the effect of alcohol addition. To study this, the series of cooks presented in Figure 44 was repeated with the difference that 50% of the cooking liquor was replaced by methanol as seen in Table 7.

**Table 7. Experimental parameters in tests on methanol impact in cooking**

	Impregnation time (min.)	Heat-up time (min.)	H-factor	Alkali charge (% EA on wood)	Methanol in cooking liquor
A.	60	2-90	2300	25	0%
B.	60	3-90	2300	25	50 %-v

The same alkali charge and H-factor were used with heat-up times from 3 to 90 minutes. A comparison between the two series is shown in Figure 49. The series without methanol is marked A, the series with methanol B.



**Figure 49. Impact of heat-up time (logarithmic scale) on delignification without (A) and with (B) methanol in cooking liquor. Kraft batch cooks, 25% EA (NaOH), impregnation 60 min 95°C, cooking H=2300 175°C.**

For the results, the following sample statistics can be calculated for the lignin yield:

$n_{water} = 8$	$n_{methanol} = 8$
$\bar{x}_{water} = 1.53$	$\bar{x}_{methanol} = 1.03$
$s^2_{water} = 0.107$	$s^2_{methanol} = 0.073$

Checking for equality of variances using a two-tailed F-test with  $\alpha$  level of .2 indicates that the variances probably are the same ( $s^2_{water} / s^2_{methanol} = 2.18$ , the critical values are  $f_{.1}(7, 7 \text{ df}) = 2.78$  and  $f_{.9}(7, 7 \text{ df}) = 0.36$  /121/.

The pooled variance can be calculated using the equation:

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \quad \text{Equation 9}$$

This yields  $s_p^2 = 0.008$

When the variance is equal the confidence interval for the difference between two means is given by:

$$(\bar{X}_1 - \bar{X}_2) \pm t_{\alpha/2} \sqrt{s_p^2 (1/n_1 + 1/n_2)} \quad \text{Equation 10}$$

using a 95% confidence interval this yields:  $(1.53 - 1.03) \pm 2.14 \sqrt{0.008(1/8 + 1/8)} = 0.5 \pm 0.1$ . In other words, the difference in mean lignin yield between a methanol and a non-methanol process with this set-up is, with 95% certainty, between 0.4 and 0.6 lignin yield percentage points. Clearly, using methanol can be considered a significant method of intensification, as the lignin yield drops by 30%.

In agreement with the findings of other researchers, a clear improvement in the attainable degree of delignification can be seen with the addition of alcohol. These first trials clearly showed that the addition of methanol to a kraft cook speeds up the process drastically, just as predicted. As far as the rejects content of the pulp is concerned, the low lignin contents used in the first trials did not produce any rejects in any case, so that question went unanswered.

The total yields of the two cases can be seen in Figure 50. Using the same procedure as before, the following statistics are obtained:

$n_{\text{water}} = 8$	$n_{\text{methanol}} = 8$
$\bar{x}_{\text{water}} = 44.5$	$\bar{x}_{\text{methanol}} = 43.7$
$s_{\text{water}} = 0.560$	$s_{\text{methanol}} = 0.320$

We now get  $s_{\text{water}}^2 / s_{\text{methanol}}^2 = 3.05$ . This indicates non-equal variances. The *Smith-Satterthwaite* procedure is used to calculate the degrees of freedom for the data:

$$\gamma = \frac{\frac{s_1^2 / n_1 + s_2^2 / n_2}{\frac{s_1^2 / n_1}{n_1 - 1} - \frac{s_2^2 / n_2}{n_2 - 1}}}{\frac{s_1^2 / n_1 + s_2^2 / n_2}{\frac{s_1^2 / n_1}{n_1 - 1} - \frac{s_2^2 / n_2}{n_2 - 1}}} \quad \text{Equation 11}$$

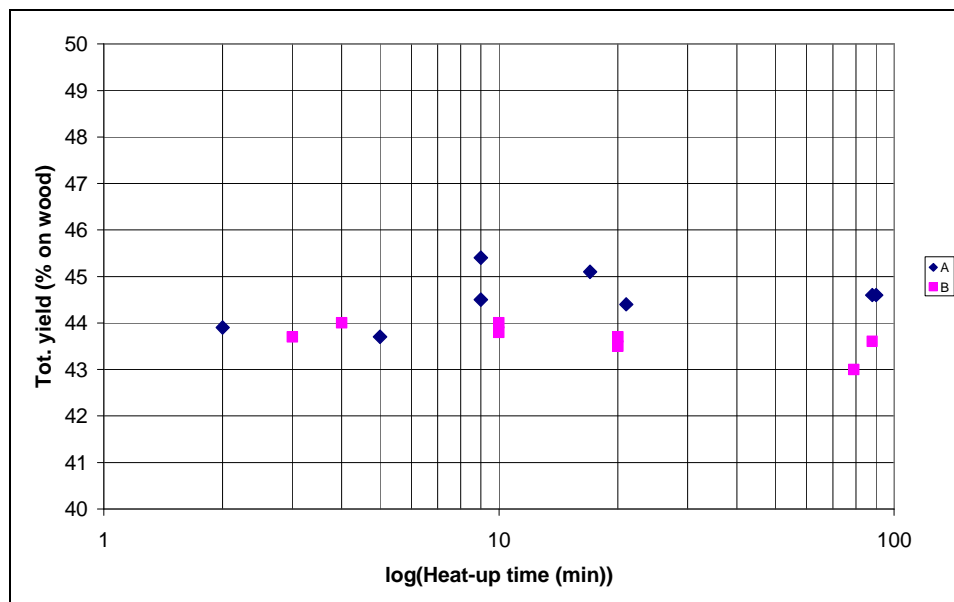
This yields 13 degrees of freedom for the data in question. The equation for confidence intervals for the difference in means for samples with unequal variance is given by:

$$(\bar{X}_1 - \bar{X}_2) \pm t_{\alpha/2} \sqrt{s_1^2 / n_1 + s_2^2 / n_2} \quad \text{Equation 12}$$

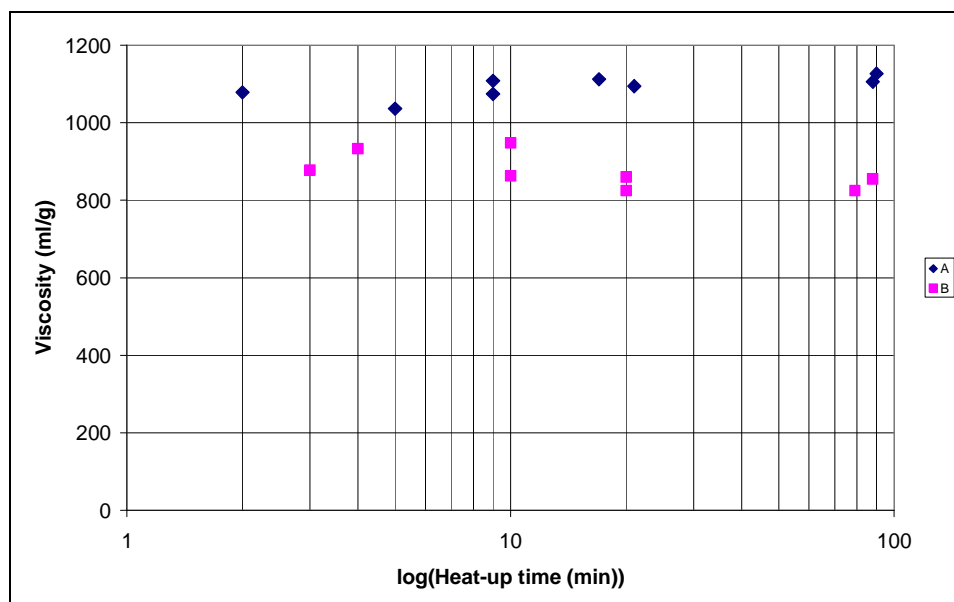


This gives  $(44.5-43.7) \pm 2.16 \sqrt{0.313/8 + 0.107/8} = 0.9 \pm 0.49$ . In other words, with 95% certainty the difference in yield is between 0.4 and 1.4 percentage points.

There is a slight tendency towards higher total yield for the non-methanol cooks, but as the lignin yield is higher in these cooks, the comparison is not completely without bias. When comparing the pulp viscosities in Figure 51, it can be seen that the methanol cooks had lower viscosity, but the heat-up time had very little impact on viscosity.



**Figure 50. Impact of heat-up time (logarithmic scale) on total yield without (A) and with (B) methanol in cooking liquor. Kraft batch cooks, 25% EA (NaOH), impregnation 60 min 95°C, cooking H=2300 175°C.**



**Figure 51. Impact of heat-up time (logarithmic scale) on pulp viscosity without (A) and with (B) methanol in cooking liquor. Kraft batch cooks, 25% EA (NaOH), impregnation 60 min 95°C, cooking H=2300 175°C.**

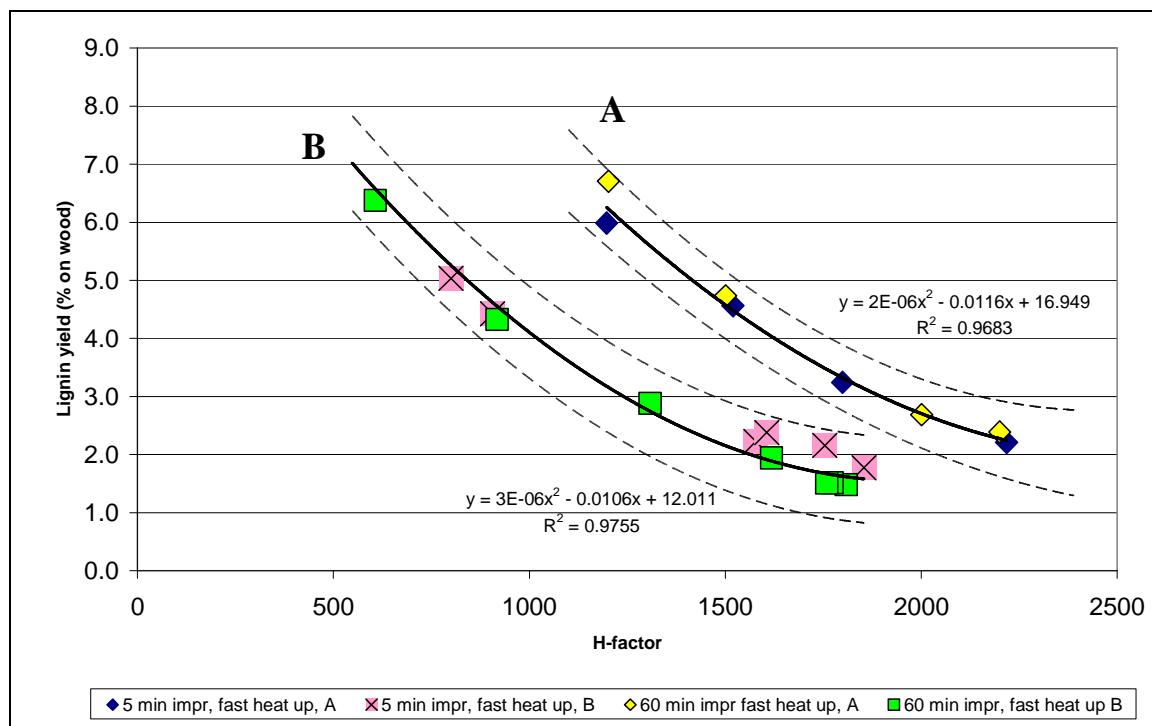
Using the same statistical procedures as above, it seems probable that the viscosity for both methods has the same variance ( $s^2_{water} / s^2_{methanol} = 0.40$ ). The calculations yield that with 95% certainty the difference in mean viscosity for the pulps is between 177 and 218 units. It has to be remembered that the pulps also have quite different lignin contents.

To clarify the impact of delignification on pulp yield with and without methanol addition, another series of cooks was undertaken. In this series the effect of short and long impregnation, in combination with fast heat-up, was tested.

**Table 8. Experimental conditions in studies on effects of impregnation and methanol addition.**

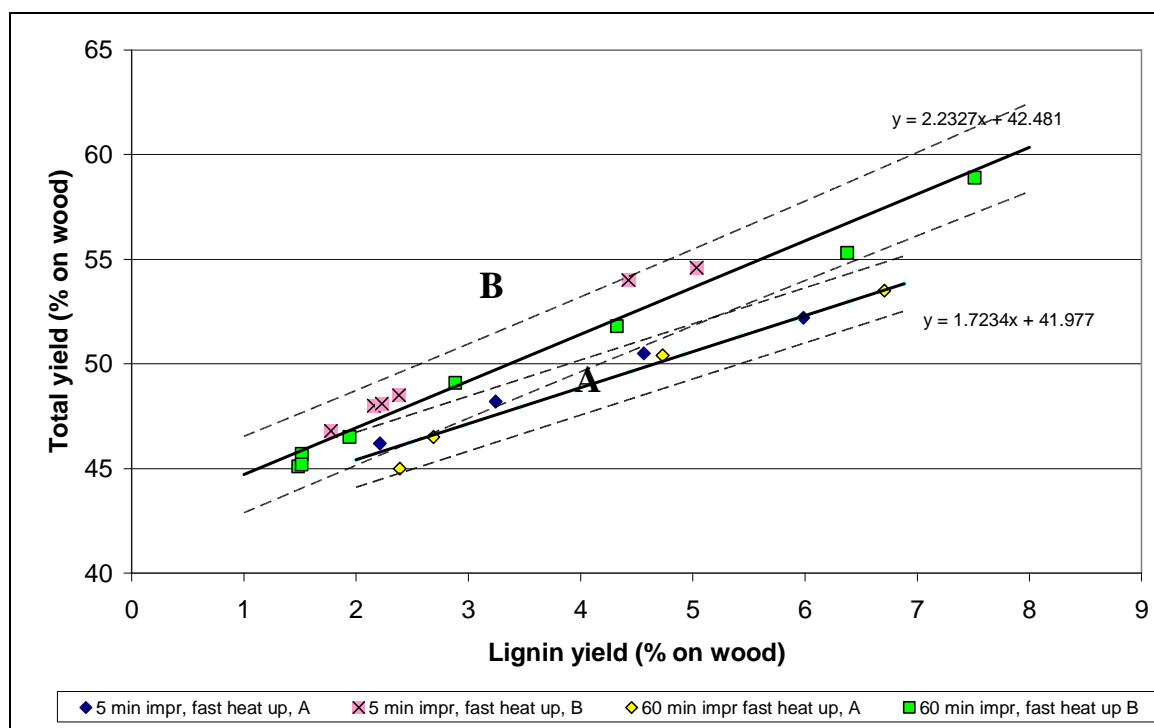
	Impregnation time (min.)	Heat-up time (min.)	H-factor	Alkali charge (% EA on wood)	Methanol in cooking liquor
A.	5	5	1400–2200	19.0-25.3	0%
	60	5			
B.	5	5	500-1800		50 %-v
	60	5			

The impact of methanol addition on delignification speed seen in Figure 52 is undisputable and covers the whole range of delignification studied. The H-factor needed to reach a given kappa number is reduced by around 50% at high lignin content and by around 30% at lower lignin contents. It seems that methanol works especially at the beginning of the cook. The results show that methanol addition can clearly be classified as a potential method for intensifying softwood kraft pulping.



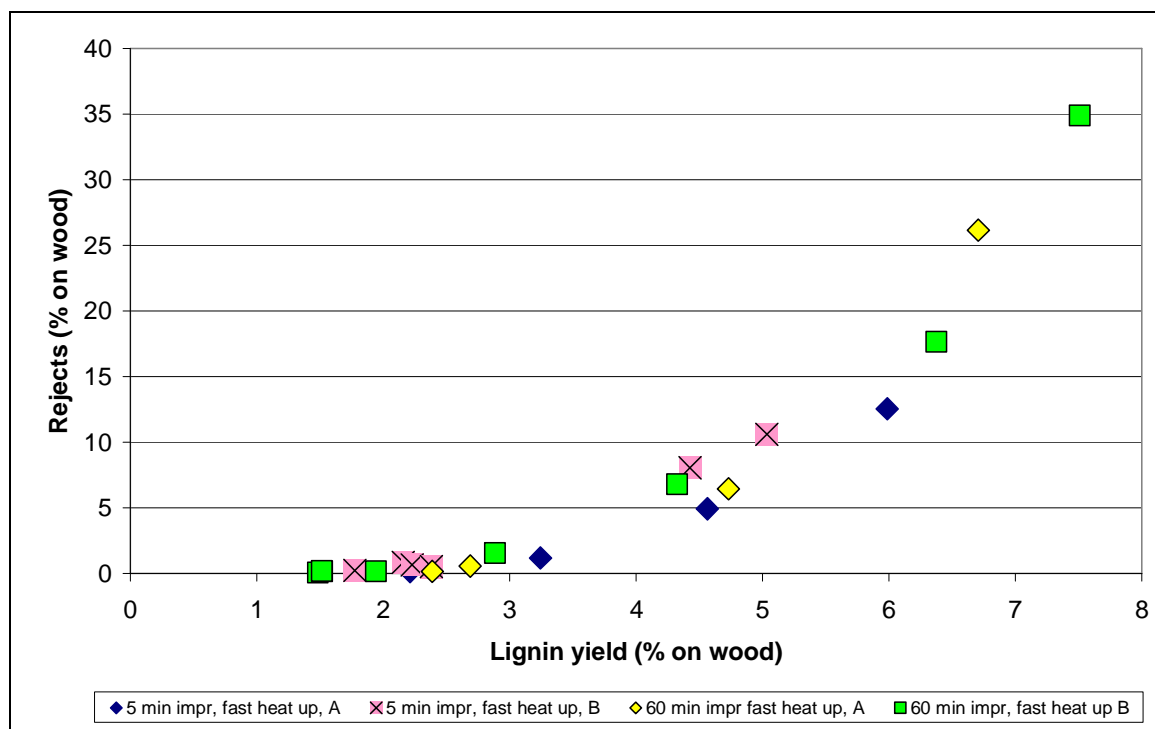
**Figure 52. Lignin yield vs. H-factor for liquid phase batch cooks using short impregnation with (B) and without (A) methanol addition. Constant end-of-cook alkalinity. 95% confidence intervals for individual values for the two methods indicated by dashed lines.**

The total yield of the methanol-containing cooks was up to 3-4 percentage points higher at delignification ranges typically used in the industry than that of the conventional process, as can be seen in Figure 53. The impact increases with rising lignin content.



**Figure 53. Total yield as a function of lignin yield for constant end-of-cook alkalinity liquid phase batch cooks without (A) and with (B) methanol addition. Constant end of cook alkalinity. 95% confidence intervals for individual values for the two methods indicated by dashed lines.**

A special area of interest was to examine if there was an effect leading to earlier softening of the lignin in the presence of an organic solvent, and if an impregnation set-up could be found that would favor such a softening. This phenomenon should be identified as low rejects levels. The length of impregnation stage could be expected to have the biggest impact on rejects, as good impregnation is said to reduce the non-uniformity of pulping. The results in Figure 54 show that the effect of impregnation time on rejects is not very big in this comparison. There is a tendency towards higher rejects in the methanol-containing cooks, but in these the pulping time is shorter due to the effect of methanol. Consequently, the higher rejects contents may in fact be explained by the shorter overall pulping time, which allows less time for diffusion of chemicals. Should the same results be presented as a function of cooking time, the methanol containing cooks would clearly have a lower reject content. However, based on these results, no evidence of softening at higher lignin contents can be seen.



**Figure 54. Rejects as a function of lignin yield for constant end-of-cook alkalinity liquid phase batch cooks without (A) and with (B) methanol addition.**

As can be seen in Figure 55, the screened yield of the methanol-containing cooks is higher than that of the non-methanol cooks up to a lignin yield of ~4% on wood. This means that the slight increase in rejects is more than compensated for by the increase in total yield.

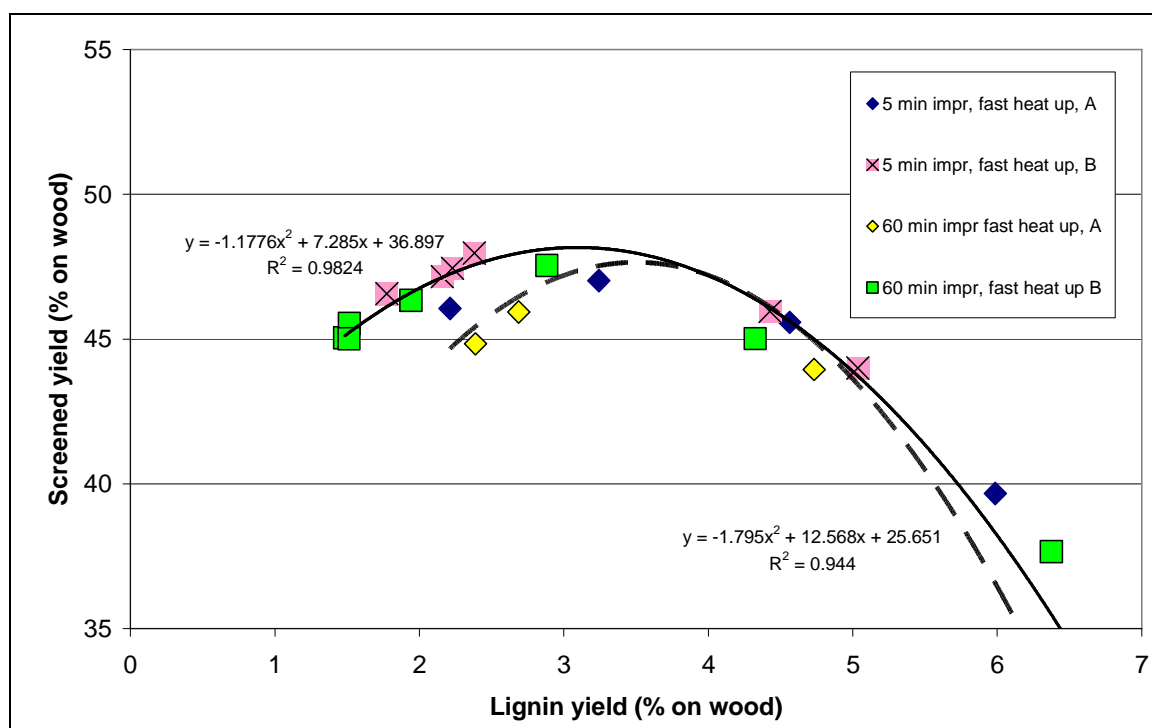


Figure 55. Screened yield vs. lignin yield for constant end-of-cook alkalinity liquid phase batch cooks without (A) and with (B) methanol addition. The trendlines are based on all cooks for both variations.

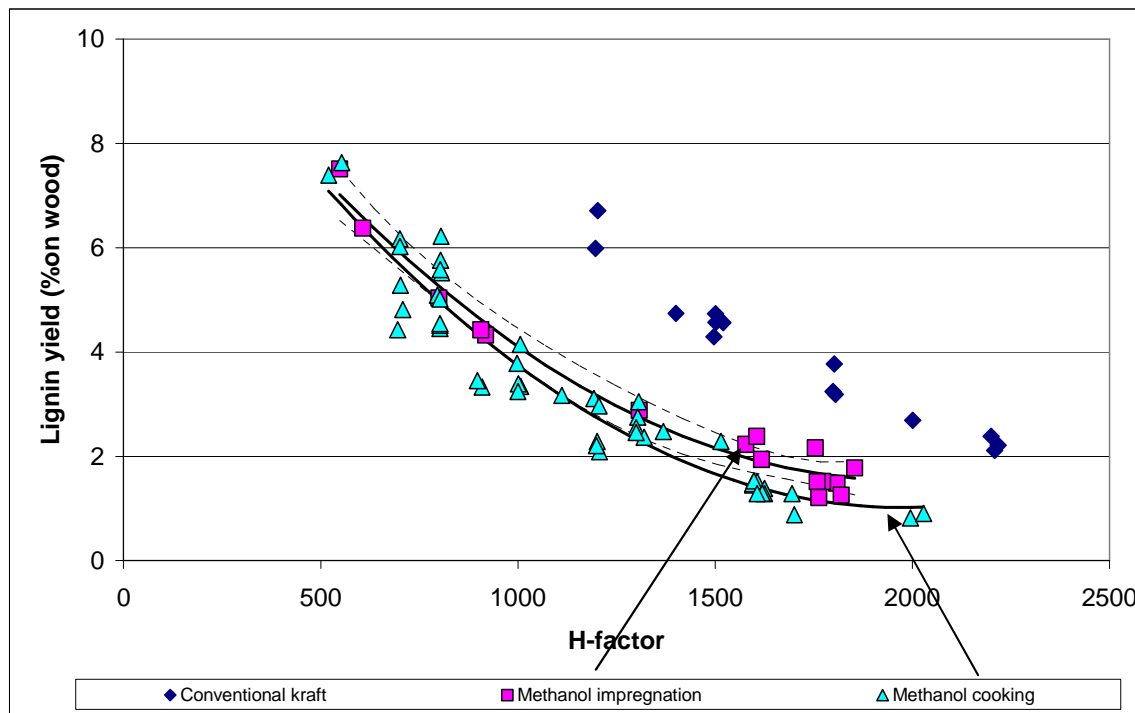
### 4.3 Impact of the allocation of methanol addition

It was clear from the batch experiments that the kinetic benefit of adding methanol to kraft pulping reported by other researchers is real. In order to understand the effect better, the first priority was to figure out if the methanol should be added in impregnation or during heat-up. If methanol is added in impregnation it will penetrate and diffuse deep into the chip together with the cooking liquor. This results in a situation where the methanol is close to the reaction sites inside the wood. In the following, cooks in which methanol has been added during impregnation are referred to as methanol impregnation cooks. On the other hand, if the methanol is added after impregnation, as a heat-up medium by displacement, there is less dilution of the methanol, but it will not penetrate as deep into the chip. This method is referred to as MeOH cooking, the impregnation having been performed with normal kraft chemicals.

Table 9. Experimental conditions for methanol impregnation and methanol displacement cooks.

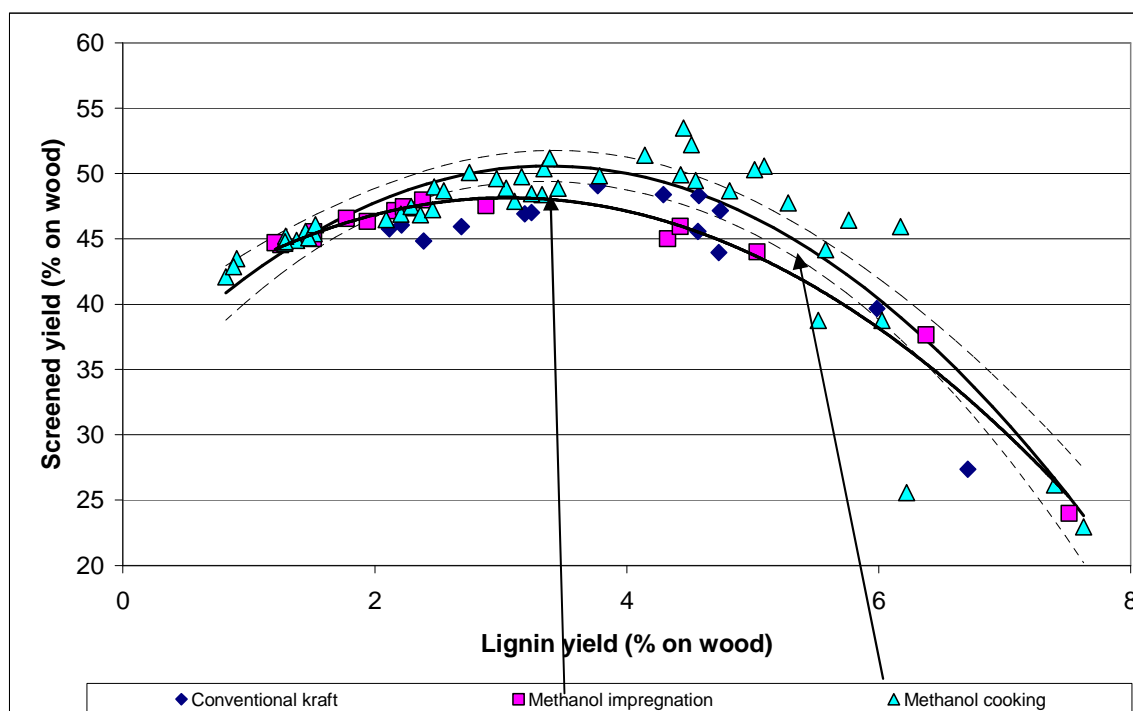
	Impr. time (min.)	Heat-up time (min.)	H-factor	Alkali charge (% EA on wood)	Methanol in impr. liquor	Cooking liquor added
Methanol impregnation	5 & 60	5-90	550 - 1820	17.0-25.3	50 %-v	No
Methanol cooking	5 min – 7 days	3-90	520 - 2030		0%	Methanol displacement

The experiments were performed using constant end-of-cook alkalinity, as explained earlier. As part of the active chemicals charged in a displacement heated cook will be present in the liquor that leaves the digester during displacement, somewhat higher chemical charges had to be used in these cases than in the batch pulping experiments. All experimental parameters can be found in the appendixes.



**Figure 56. Lignin yield as a function of H-factor for conventional batch kraft, methanol impregnation (methanol part of impregnation liquor) and methanol cooking (kraft impregnated chips displacement heated using methanol) pulping methods with constant end-of-cook alkalinity. Dashed lines indicate 95% confidence bound for mean of methanol impregnation method.**

From the point of view of process speed, there seems to be virtually no difference between the case where methanol is present in impregnation and that where it is brought in as the heating liquor in the actual cooking stage, as is seen in Figure 56. The average degree of delignification for the methanol displacement cooking method is for most of the range within the 95% confidence bound of the mean of the methanol impregnation method. This is in fact rather surprising, as it is highly unlikely that methanol could penetrate very deeply into a chip that has already been impregnated with cooking chemicals, as is the case in MeOH cooking. The fact that there still is an effect supports the theory that the effect is not dependent on methanol taking part in delignification chemistry.



**Figure 57. Screened yield as a function of lignin yield in constant end-of-cook alkalinity cooks with different pulping methods. 95% confidence interval for mean value for methanol cooking shown.**

Looking at the same pulping methods from the point of view of yield optimization, solvent displacement heating offers a clear benefit over both conventional batch kraft and methanol-containing batch kraft pulping. The improved screened yield seen in Figure 57 was due to a combination of low rejects and high total yield. These results indicated superior defibration, which is reflected as low rejects for the methanol displacement process, as predicted earlier. Also, the benefit of methanol addition does not seem to be reaction chemistry based, as the methanol is not present at the reaction sites in the chip interior.

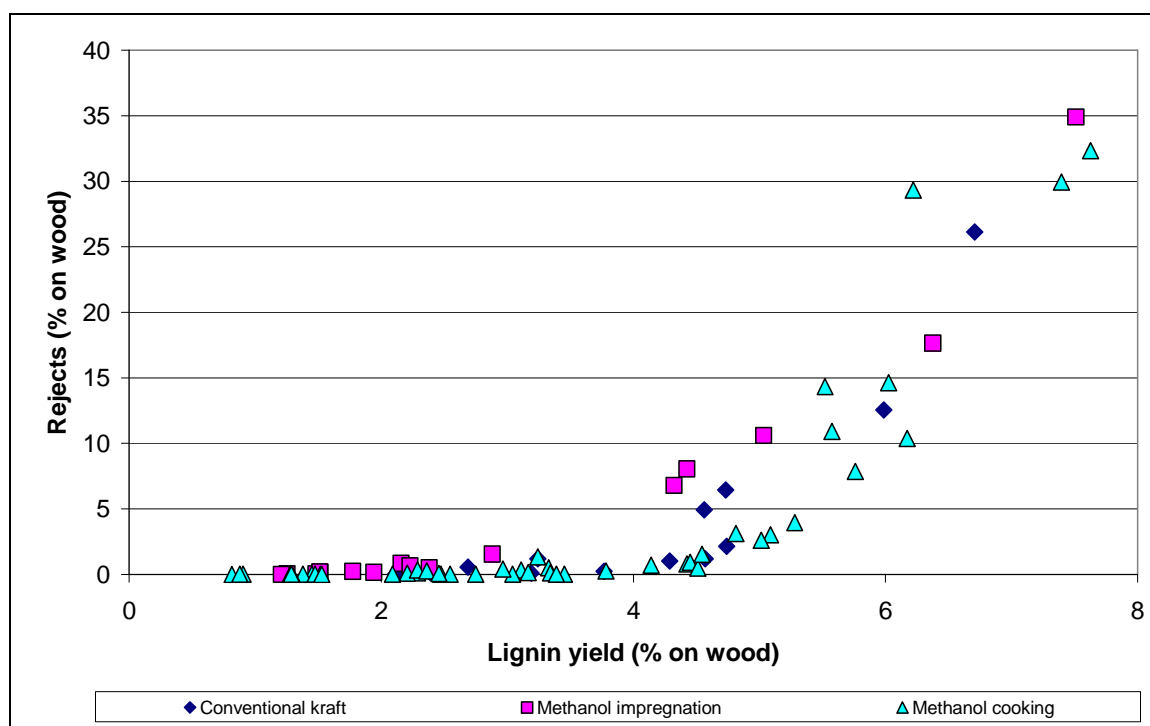


Figure 58. Rejects vs. lignin yield in constant end-of-cook alkalinity cooks with different pulping methods.

#### 4.4 Reducing the amount of methanol

Concluding that displacement heating (the methanol cooking method) was as fast as the methanol impregnation method but gave higher screened yield, it was chosen for further study. The question soon arose what the minimum amount of methanol would be to bring about this positive effect. When looking for means to answer this question, the idea to use only methanol vapor for heating was brought up.

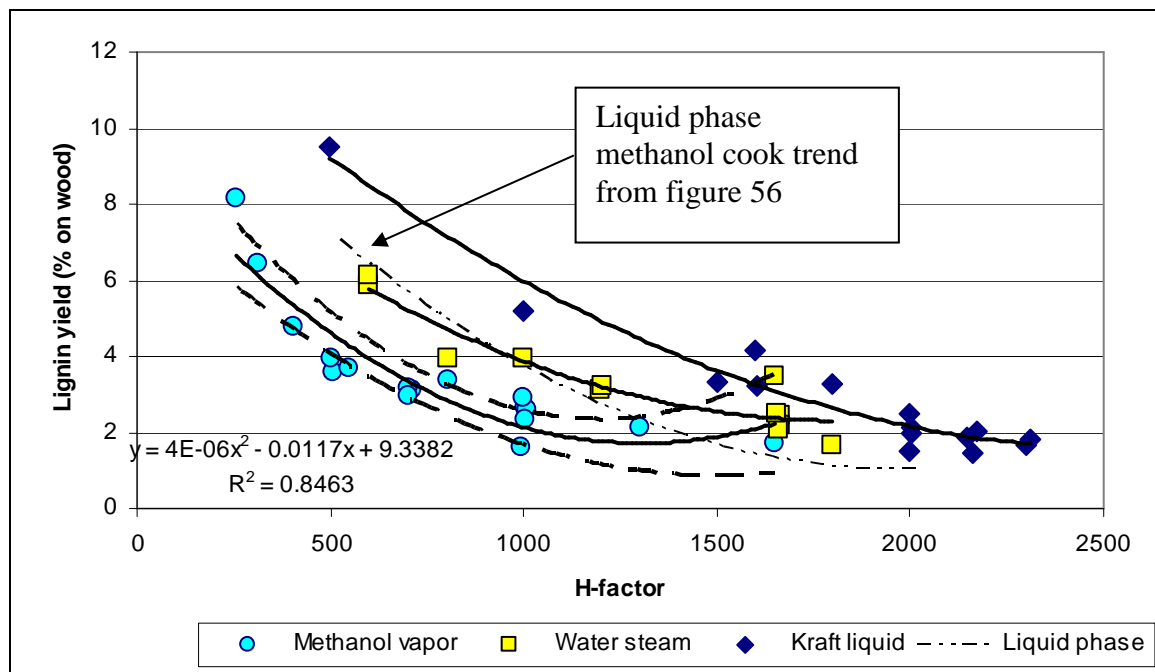
A series of cooks was performed in which the impregnation was performed much in the same way as in the methanol displacement cooks. After impregnation, the free liquor was removed as effectively as possible by blowing nitrogen gas through the system. Heating was then started by introducing an amount of methanol that was only sufficient to fill the push-pull cylinder, and the jacket temperature was raised as fast as possible. By pumping the methanol back and forth through the heating coil ahead of the digester, the heat was transferred to the chips as methanol was vaporized and condensed on the chips, as explained in the experimental section.

Table 10. Experimental scenarios in vapor phase pulping experiments.

	Impr. time (min.)	Heat-up time (min.)	H-factor	Alkali charge (% EA on wood)	Impregnation liquor c. (g NaOH/l as EA)
Water steam phase	60	5-7	600-1800	40-43	95-107
Methanol vapor phase			250-1650	38-45	90-120



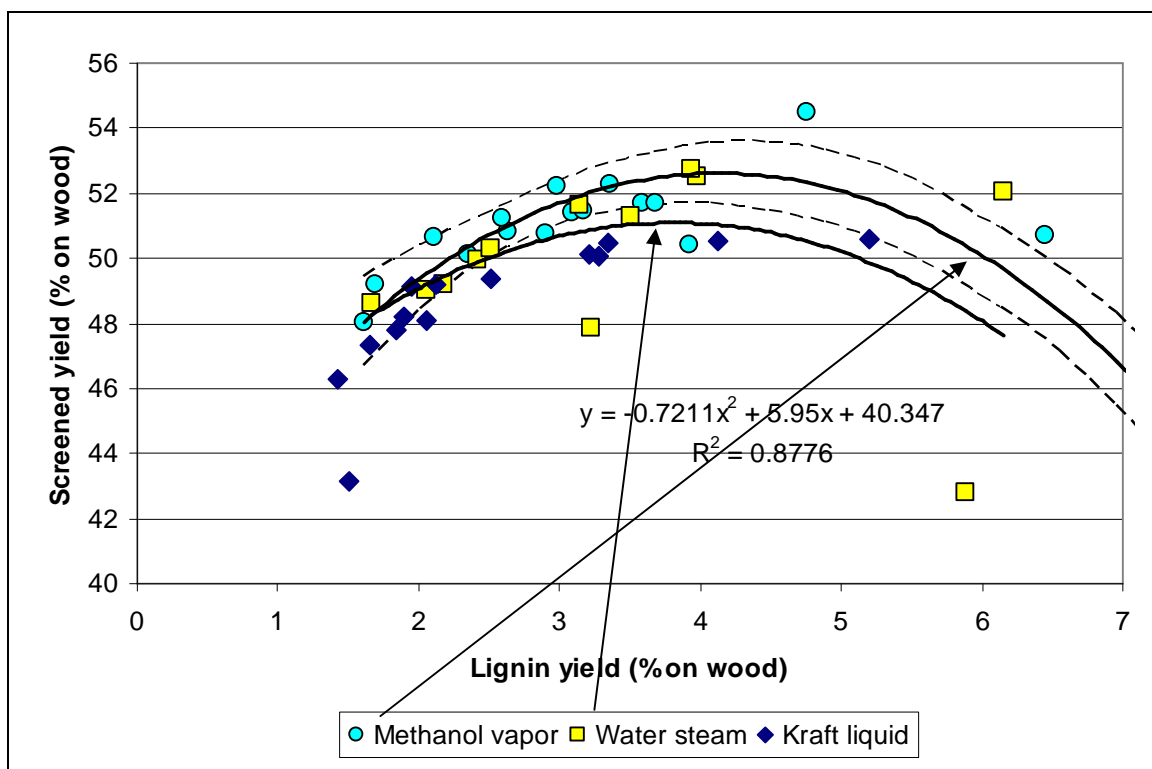
As the end-of-cook alkalinity was kept constant and all chemicals had to be transferred in the impregnation stage, it was quickly realized that the strength of the impregnating liquor had to be increased to allow vapor phase pulping. Liquors up to EA 120 g NaOH/l had to be used to give enough alkalinity to reach low lignin contents. If lower alkalinity was used, the cooking slowed down towards the end of the cook and any possible benefit was lost.



**Figure 59. Lignin yield vs. H-factor for softwood vapor phase pulping (liquid phase kraft shown as reference). Dotted line indicates speed of pulping for liquid phase methanol pulping (as shown in figure 56). 95% confidence interval for mean value of methanol vapor cooking method shown.**

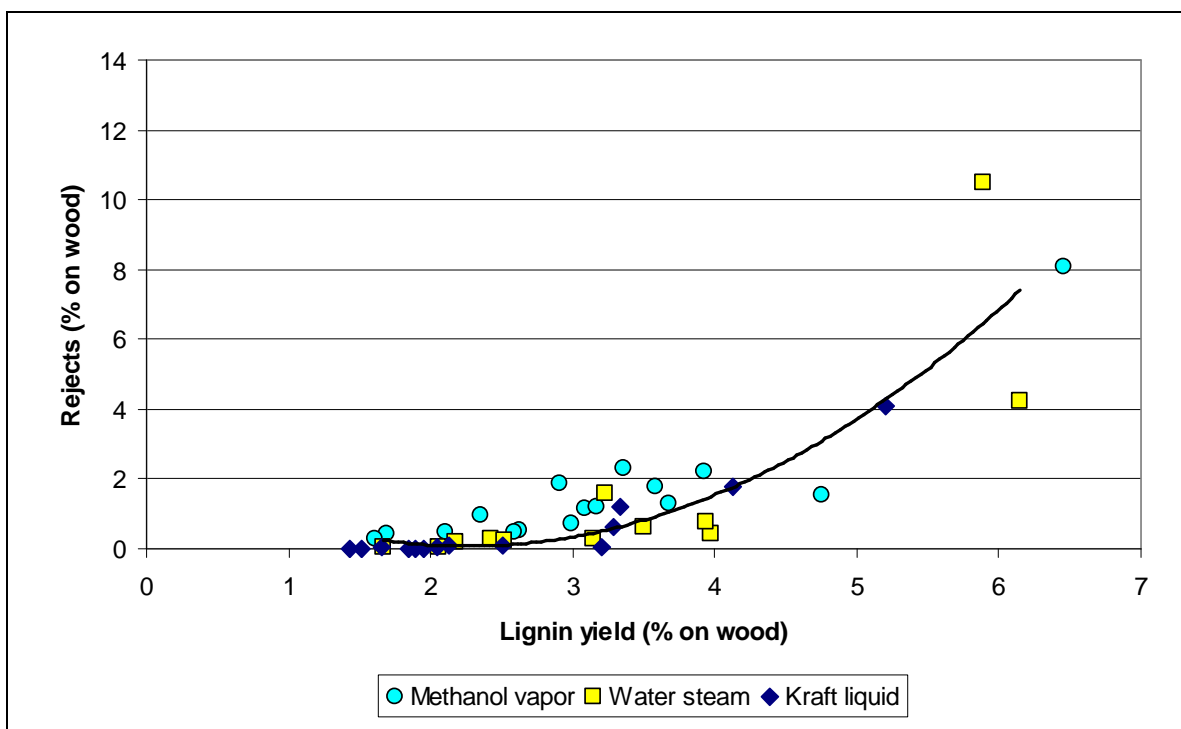
Figure 59 shows the extent of delignification achieved with the different pulping methods as a function of cooking time. If impregnation is sufficient, methanol vapor phase pulping is significantly faster than the other pulping methods. The difference is especially marked for the high lignin content range. The same experiments were also performed using water steam. Water steam phase pulping is clearly also faster than regular batch kraft pulping, but not quite as fast as methanol steam phase pulping. Interesting is also that a decrease in the amount of methanol used increased the pulping speed, as is seen when comparing the results for methanol vapor phase cooks with the line describing the methanol liquid phase (both impregnation and displacement) cooks. This is somewhat counterintuitive. If methanol were an active chemical in the actual cooking reactions then the opposite would be expected as the charge and thus overall concentration of methanol is smaller in the vapor phase cooks.

The results shown in Figure 59 are quite remarkable, as they clearly show that the solvent effect is independent of the amount of solvent charged. The results indicate that the action of the methanol is only to transfer heat and modify the reaction environment, it is not taking part in the actual reactions.



**Figure 60. Screened yield vs. lignin yield for softwood vapor phase pulping methods, liquid phase conventional kraft shown as reference. 95% confidence interval for mean value shown in methanol vapor phase cooking.**

Figure 60 shows the screened yield as a function of lignin yield for the pulping methods studied. There is a fair amount of scatter in the results, especially for the high lignin content range, but with methanol vapor phase pulping the yield is clearly quite good. Not only was methanol vapor phase pulping fully possible, it also gave an extra benefit in process speed and yield in the lignin yield range of 2-4 % on wood. However, at higher lignin yields the results become unreliable as it is hard to ensure proper pulp disintegration. In any case, the available points certainly do not rule out a higher yield for methanol vapor phase pulping.



**Figure 61. Rejects vs. lignin yield for softwood vapor phase pulping methods. Liquid phase conventional kraft shown as reference.**

Figure 61 indicates a slightly higher level of rejects for methanol vapor phase pulping than for either liquid phase or steam phase kraft pulping. With this in mind the high screened yield seen for methanol vapor phase pulping is even more remarkable.

The fact that methanol steam can be used successfully substantially reduces the amount of methanol needed compared to a process with liquid phase displacement heating. In the continued research, vapor phase pulping became the “state-of-the-art” pulping method and the subject of further study. In the reminder of the work, the methods that are compared to each other are kraft liquid phase pulping as a basic reference, water steam phase as a reference for a known “high speed” pulping method and methanol vapor phase pulping as the new experimental cooking method.

#### **4.5 Impregnation in methanol vapor phase pulping**

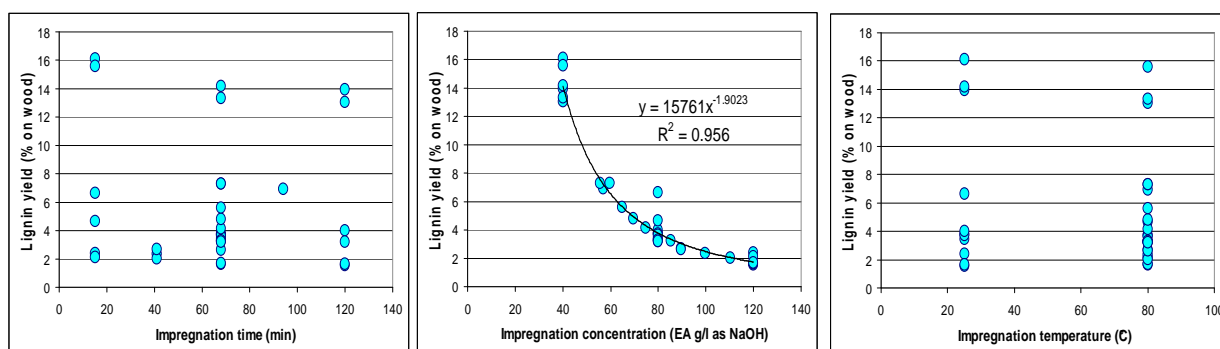
According to the experiments, displacement heated pulping was faster than batch pulping and steam phase pulping faster than displacement heated pulping, whereas methanol gave an extra advantage in all cases. The biggest practical difference between batch, displacement and vapor phase pulping lies in impregnation. As methanol vapor phase pulping was the fastest method so far, further experiments were performed to clarify the impact of impregnation on this process.

The parameters in impregnation are time, temperature and concentration. Tests were performed with different times, two different temperatures and several different concentrations as seen in Table 11. The L:W-ratio in impregnation and cooking time were kept constant. This naturally leads to varying end-of-cook alkalinity, in some cases zero, in some cases quite high. The idea was merely to study the effect of changing the impregnation concentration on the end result.

**Table 11. Experimental conditions in studying the effect of impregnation on methanol vapor phase pulping.**

	Impr. time (min.)	Heat-up time (min.)	H-factor	Alkali charge (% EA on wood)	Impregnation liquor c. (g NaOH/l as EA)
Methanol vapor phase	15, 40, 68, 94, 120	5-10	1000	17-51	40-120

The cooking result in terms of lignin yield is shown as a function of impregnation time, concentration and temperature in figure 62.

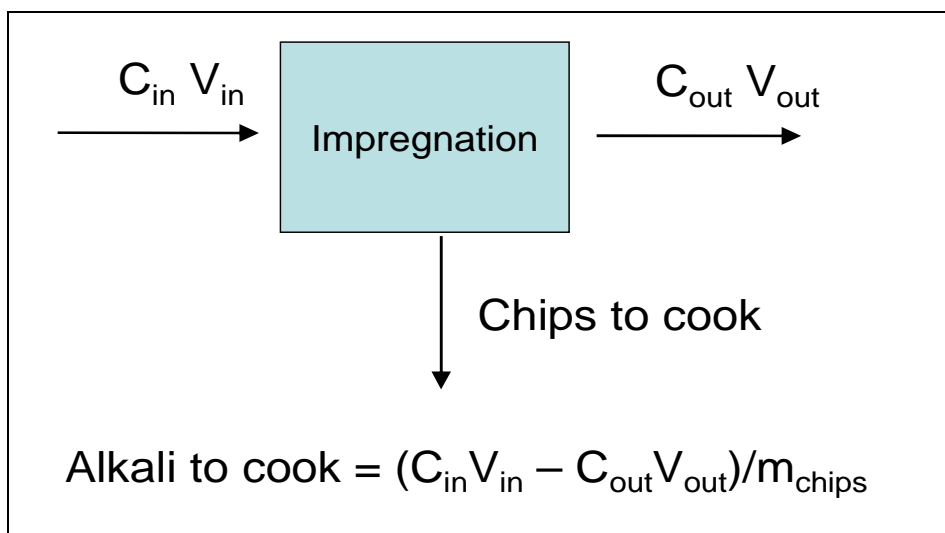


**Figure 62. Scatter plot of lignin yield vs. impregnation time, concentration and temperature for cooks with varying impregnation conditions but constant cooking (H=1000, t=175°C, methanol vapor phase)**

Looking at figure 62 it is clear that most of the variation in the cooks is explained by the impregnation concentration. The correlation coefficient between the two is 0.956, so it is clear that the concentration is very important. However, there are some outliers that do not quite fit the model. Also, as the liquor to wood ratio was the same in all experiments the results are somewhat misleading.

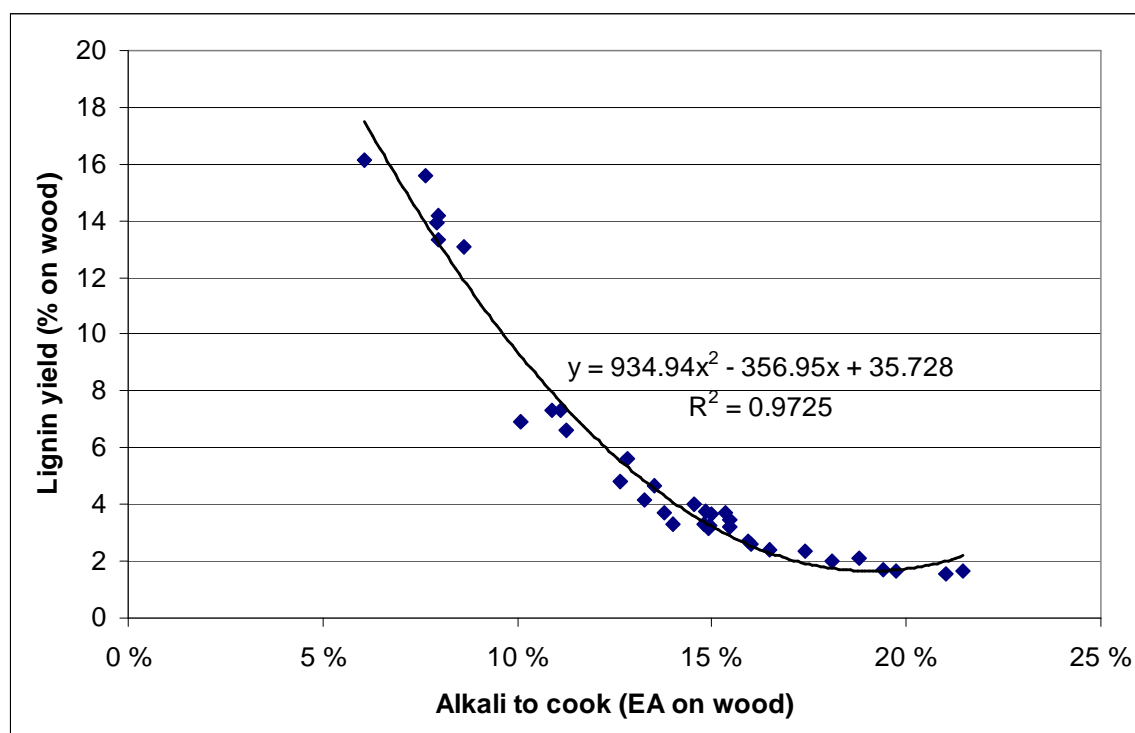
In an attempt to devise a model that explains the outcome even better it was felt that there should be some parameter taking into account also the impact of temperature and time. To describe the amount of alkali transferred to the wood during impregnation the concept of “alkali to cook” was introduced. Alkali to cook was defined as shown in figure 63. The idea of the alkali to cook measurement is simply to give an idea of the efficiency of impregnation. The theory being that since no mass transfer happens during the reaction stage in vapor phase pulping, all alkali has to be transferred during the impregnation step and some measure of the efficiency of this is needed.

An important point is that alkali to cook includes that amount consumed in chemical reactions during the impregnation step. This signifies that the concept may not be so clear cut for processes with significantly higher impregnation temperatures.



**Figure 63. The definition of alkali to cook**

In Figure 64 the same data as in Figure 62 are viewed as a function of alkali to cook. Clearly the new parameter has an even higher correlation with achievable lignin yield.



**Figure 64. Lignin yield. vs. alkali to cook for cooks with varying impregnation conditions but constant cooking (H=1000, t=175C, m ethanol vapor phase)**

Overall cooking speed (disregarding the fact that cooking stops when alkali is depleted) can clearly be predicted by alkali to cook.

#### 4.5.1 Process yield of intensified methanol vapor phase pulping

A fast process is interesting only if it gives at least as high yield as a slow one. In contemporary pulping research, high alkali charges are always seen as unrealistic as they lead to lower yield. Figure 65 shows a surprising effect for methanol vapor phase pulping using different amounts of alkali in the cooking stage. The total yield of the process decreases with increased delignification achieved by higher alkali to cook, as expected. However, the lignin free screened yield actually seems to be improving slightly. The rationale behind the use of lignin free screened yield is that this is the material that is interesting from a papermaking point of view. Any lignin that is left after pulping will be removed in bleaching. Based on this result it seems that methanol vapor phase pulping can be used to reach very low lignin contents in pulp without sacrificing brownstock yield.

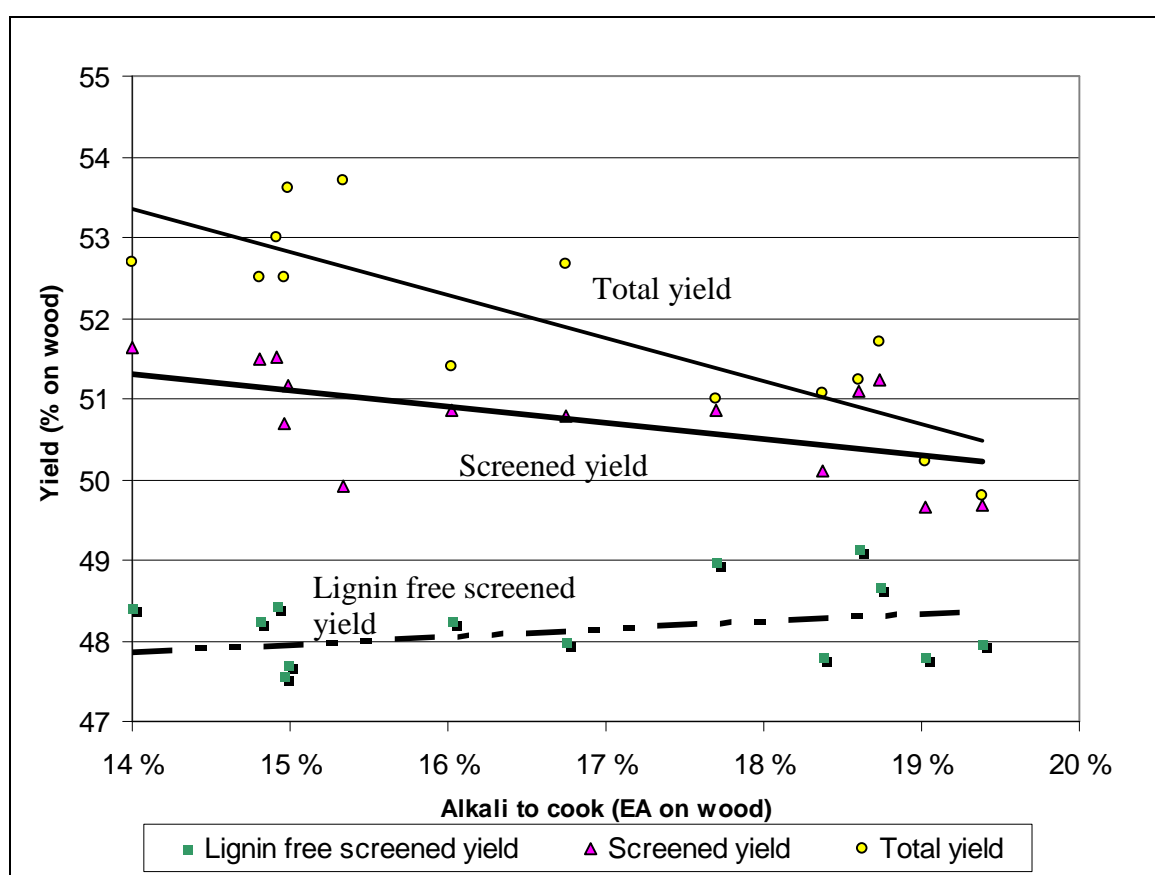


Figure 65. Total yield, screened yield and lignin free screened yield for cooks with varying impregnation conditions but constant cooking ( $H=1000$ ,  $t=175^{\circ}\text{C}$ , methanol vapor phase). Lignin yield at alkali to cook 14% = 4.1% on wood, at 19% lignin yield = 1.6%.

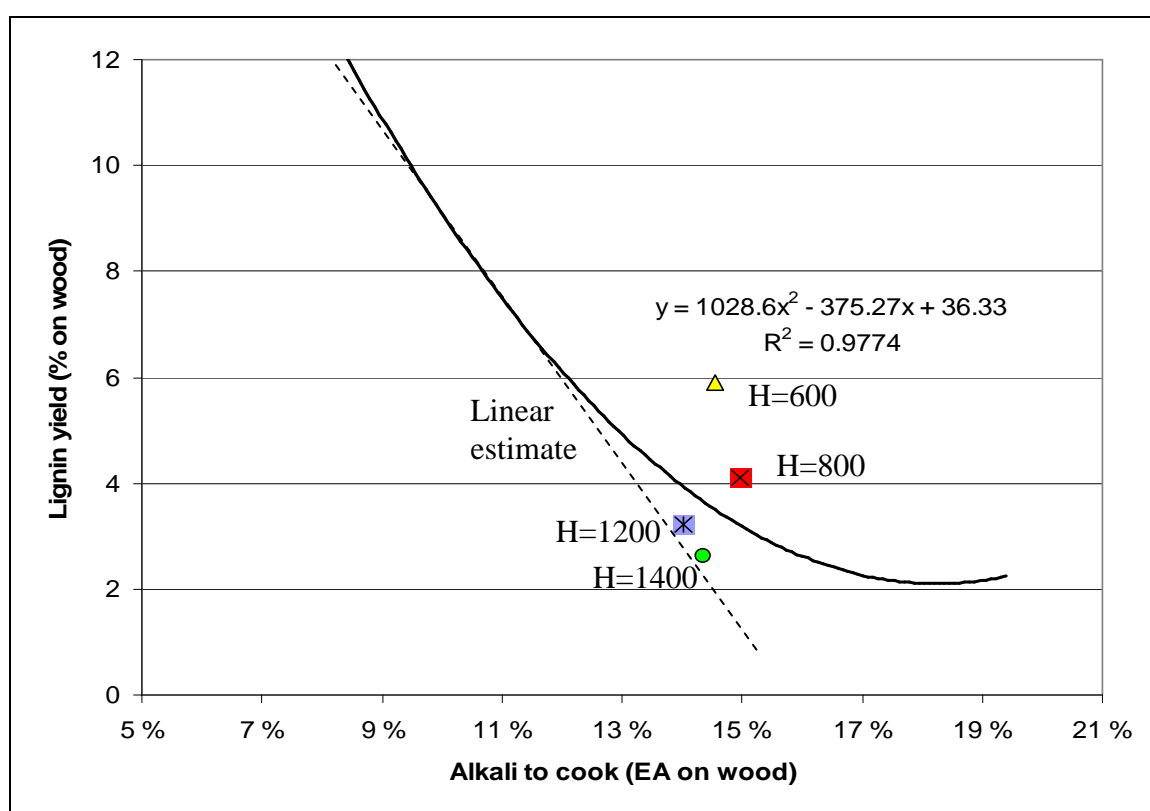
#### 4.5.2 Alkali to cook and cooking time

To further study the interdependence of alkali to cook, cooking time and degree of delignification, additional tests were performed. In these tests the cooking time was varied while keeping all other parameters constant. Based on the earlier experiments the impregnation was expected to correspond to an alkali to cook of ~15% on wood.

**Table 12. Experimental conditions in study on the effect of the cooking time on achievable delignification with constant impregnation.**

	Impr. time (min.)	Heat-up time (min.)	H-factor	Alkali charge (% EA on wood)	Impregnation liquor c. (g NaOH/l as EA)
Methanol vapor phase	68	5	600, 800, 1200, 1400	34	80

The results are shown in Figure 66. As can be expected, a longer cooking time leads to more delignification and a shorter time to less. The interesting thing to note is how the points relate to a hypothetical continuation of the linear part of the delignification curve for the 1000 H-factor cooks. The longer cooks fall onto the same trend and again seem to have become restricted by alkali to cook rather than cooking time.



**Figure 66. Trend of H-factor 1000 cooks compared to cooks with varying H-factor. Linear estimate for “alkali limited region” added.**

The figure also highlights a problem in the experimental setup. Although the procedure in impregnation was exactly the same in all experiments, the alkali to cook achieved varied from 14.0 % to 15.0 % on wood. The variation is due to slight differences in the amount and concentration of the liquor removed after impregnation.

#### 4.5.3 General impact of impregnation on pulping speed

The amount of alkali transferred in impregnation is the key factor for process speed and delignification in vapor phase pulping. This is obvious as there is no transfer of chemicals in the cooking stage. The experiments with liquor phase cooking indicated that

impregnation also plays a role for process speed in those methods, with displacement heating being faster than batch cooking.

In order to clarify the situation, the data for the different cooking methods were studied further. Cooks to the same delignification degree with reasonable positive end-of-cook alkalinity were selected both with and without methanol addition. By making some basic assumptions, the amount of alkali transferred in impregnation can be calculated.

In making the calculations the following assumptions were made:

- 5 minutes' impregnation gives mass-transport only by penetration
- 60 minutes' impregnation gives penetration and complete diffusion
- No consumption of chemicals during impregnation

These are seen as reasonable assumptions as the chips were well steamed and the impregnation temperature was  $>80^{\circ}\text{C}$ . The assumption regarding the consumption of chemicals is questionable, but as it is the same for all cases, it only affects the absolute numbers, not the relative differences.

This gives the following equations for calculating the charge of alkali transferred in impregnation:

$$\text{Transferred in penetration: } \frac{\left( \frac{m_{\text{wood}}}{\rho_{\text{wood}}} - \frac{m_{\text{wood}}}{\rho_{\text{w.solid}}} - \frac{m_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} \right) \times c_{\text{impr}}}{m_{\text{wood}}} \quad \text{Equation 13}$$

$$\text{Transferred in penetration and diffusion: } \frac{\left( \frac{m_{\text{wood}}}{\rho_{\text{wood}}} - \frac{m_{\text{wood}}}{\rho_{\text{w.solid}}} \right) \times c_{\text{impr}}}{m_{\text{wood}}} \quad \text{Equation 14}$$

Where:

$m_{\text{wood}}$  = chip sample weight

$\rho_{\text{wood}}$  = wood basic density ( $411 \text{ g/dm}^3$  for the softwood used)

$\rho_{\text{w.solid}}$  = density of solid wood ( $1500 \text{ g/dm}^3$  used)

$m_{\text{H}_2\text{O}}$  = weight of water in fresh wood

$c_{\text{impr}}$  = concentration of impregnation liquor



**Table 13. Cooks used in comparison of methanol free cooks, cooking temperature 175°C, lignin yield 2.35±0.15**

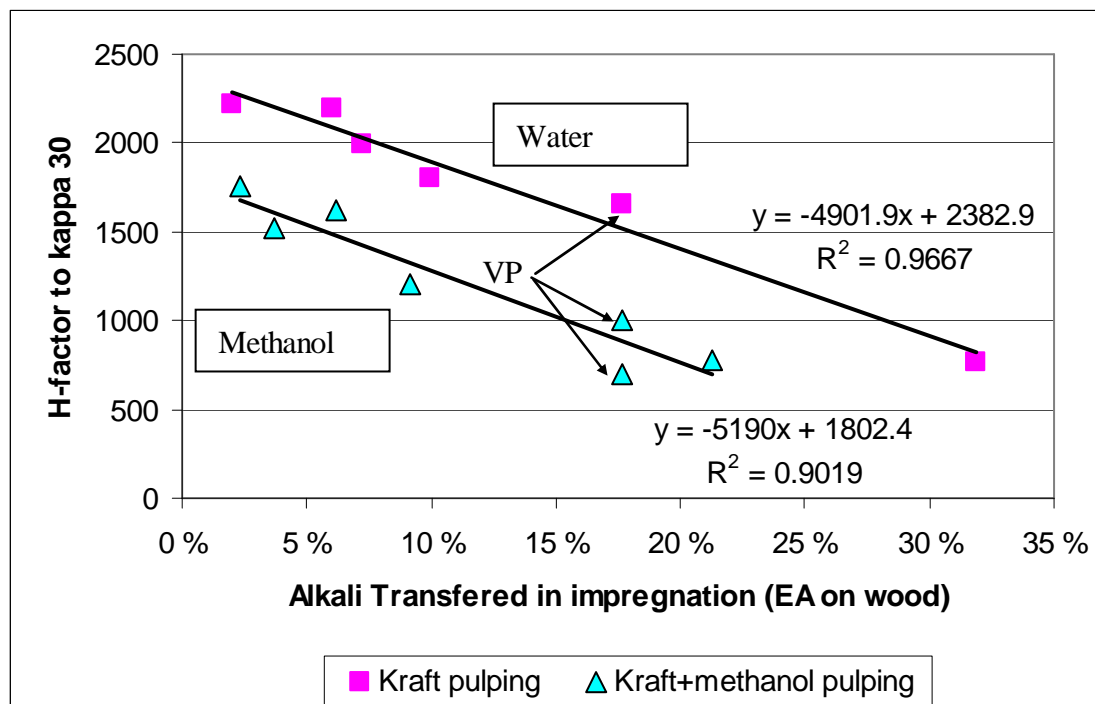
<b>Cook no.</b>	<b>Impr. time (min.)</b>	<b>Heat-up time (min.)</b>	<b>Impr. liquor conc.</b>	<b>Cooking method</b>	<b>H-factor</b>	<b>End of cook EA at pH 11</b>
94	5	5	34	Batch L:W=6.25	2218	6.3
128	60	4	34	Batch L:W=6.25	2200	6.6
310	60	5	41.0	Batch L:W=5	1998	5.7
120	60	5	56.2	Displ. heated	1803	7.1
455	65	5	100.0	Steam phase	1654	5.2
274	60	5	180.4	Drained after impr. l-phase cooking	764	26.3

**Table 14. Cooks used in comparison of methanol cooks, cooking temperature 175°C, lignin yield 2.2±0.2**

<b>Cook no.</b>	<b>Impr. time (min.)</b>	<b>Heat-up time (min.)</b>	<b>Impr. liquor conc.</b>	<b>Cooking method</b>	<b>H-factor</b>	<b>End of cook EA at pH 11</b>
118	5	4	34.4	Batch	1754	4.8
88	60	5	34.8	Batch	1618	6.7
123	60	90	51.6	MeOH displ	1207	6.4
126	5	5	54.2	MeOH displ	1515	4.8
447	65	5	100.0	Vapor phase	1002	6.0
542	1080	4	100.0	Vapor phase	699	11.2
270	60	6	120.4	Drained after impr. l-phase cooking	779	n.a.

The result of using equations 11 and 12 on the data in Table 13 and Table 14 is shown in Figure 67. This graph illustrates the cooking time needed to reach kappa number 30 with various impregnations. The result is a graph with cooking time (H-factor) as a function of how much alkali is assumed to have been transferred to the wood prior to heat-up. The rest of the alkali needed to reach kappa number 30 with positive end-of-cook alkalinity is in the surrounding liquor. There are also points for both water and methanol vapor phase heating to give an idea of the impact of using vapor phase pulping. The point

with 180 g/l does not fall into the range of accepted end-of cook alkalinity, but was added to illustrate the linearity of the trend even at higher alkali amounts.



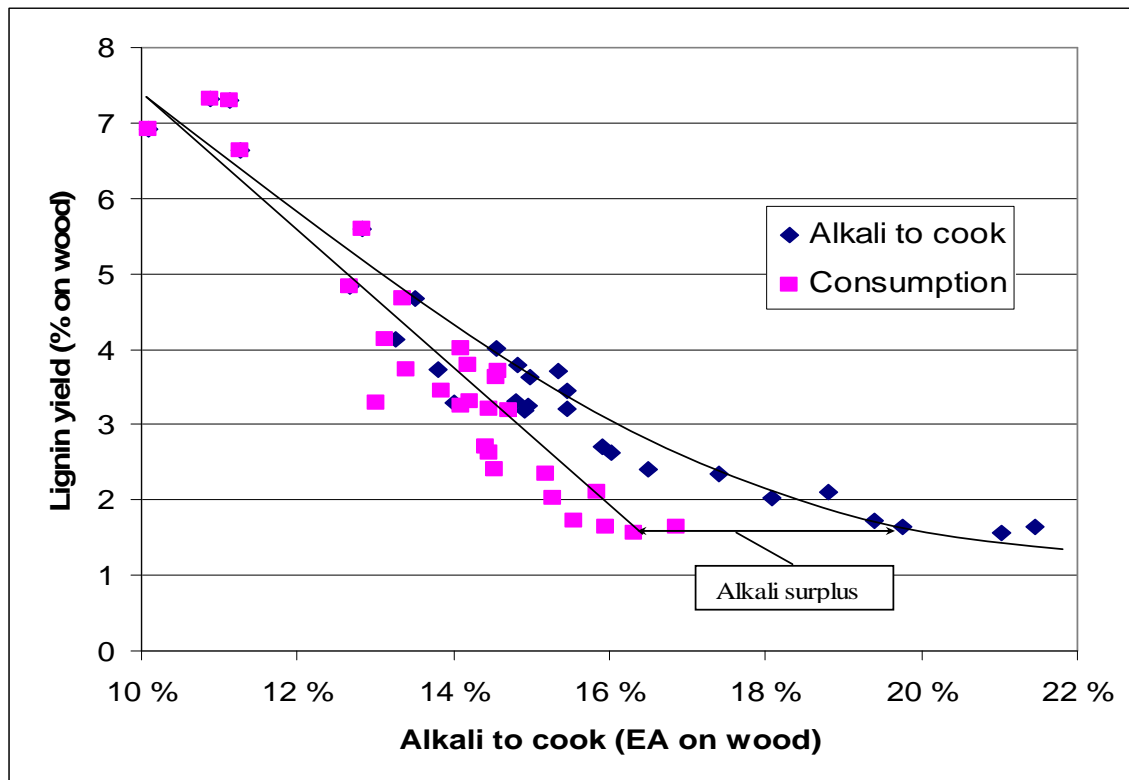
**Figure 67.** H-factor needed to reach kappa number 30 as a function of the alkali transferred into the wood prior to heat-up. All cooks have positive end-of-cook alkalinity, the rest of the alkali (in the cases where total consumption is not covered by impregnation) is in the surrounding liquor in the liquor phase cooks.

According to the figure, a similar pattern is seen both for methanol and non-methanol cooks. A 30% reduction in cooking time can be achieved by having the chemicals close to the reaction sites at the onset of the reactions. The benefit of using methanol in pulping is of the same magnitude. There is some uncertainty in the figures due to experimental variations as described earlier, but the linearity of the correlations for both cooking methods is striking. The vapor phase results fall on the same line as the results of the liquid phase cooks, this indicates that vapor phase as such does not increase pulping speed but it is a way to make sure that enough alkali has been transferred in the impregnation step to ensure a fast cook.

#### 4.5.4 Alkali consumption

The alkali transferred to the wood determines the speed and extent of reactions. Figure 65 showed that the lignin free yield is unchanged from lignin yield 2% to 4% when pulping with different alkali to cook but constant cooking time. This leaves the question of alkali consumption in cooking.

In Figure 68 the alkali to cook and the alkali consumption for different degrees of delignification are shown in the same graph. In this graph the point where the series start to move away from each other illustrates the point where the cooks go from being alkali-deficient to being time-deficient. It can also be seen how the alkali surplus needed to reach lower lignin contents becomes ever bigger unless the reaction time is increased.



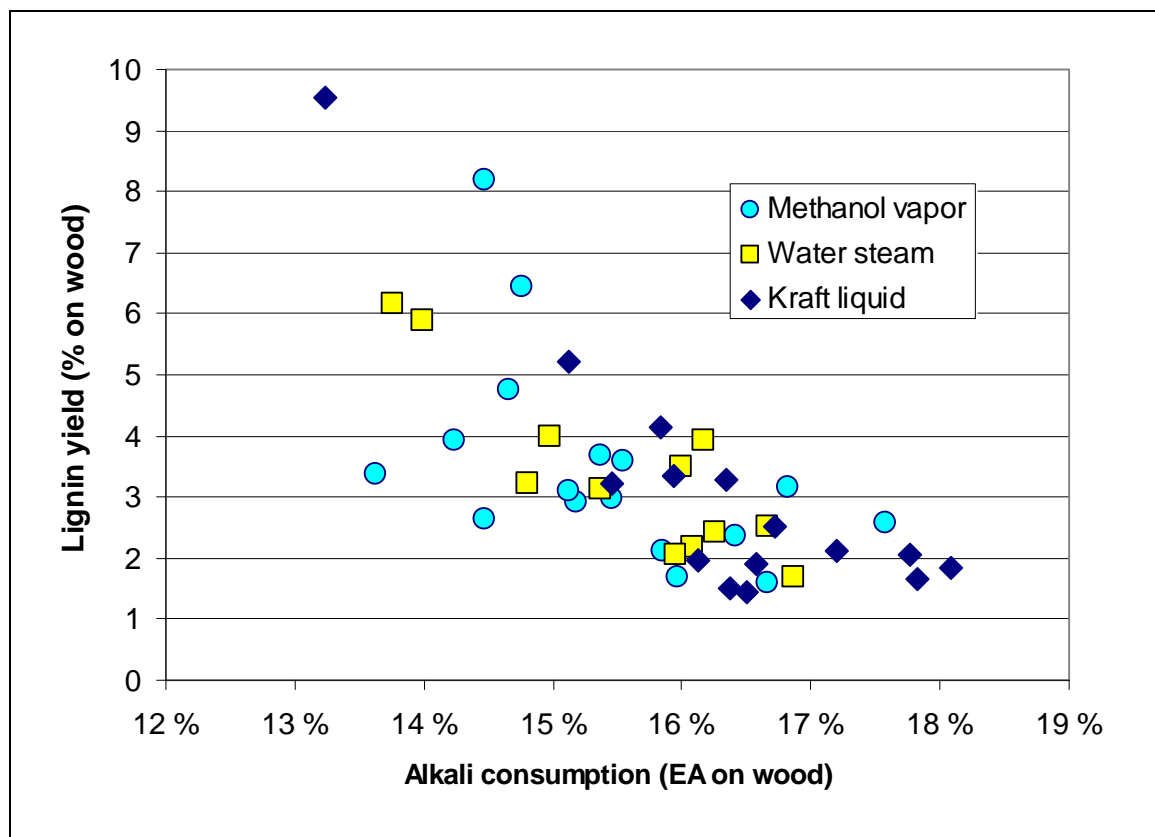
**Figure 68. Achievable lignin yield vs. EA consumption and EA to cook with constant H-factor ( $H=1000$ ) and methanol vapor phase pulping.**

According to the present trials, it seems impossible to give a strict limit for how fast methanol aided kraft pulping can be. As an example it can be mentioned that in trials with 180 g/l impregnation, giving an alkali to cook of 21%, a lignin yield of 1.4 % on wood was reached with 750 H-factors, while maintaining a yield of 49.3% on wood. This, however, gives a very high EoC alkalinity and is therefore not interesting from more than a scientific point of view. An even higher concentration seems possible to use from a yield point of view, but is far from realistic with current recovery technology in which the mill white liquor is rarely over 120 g/l. The use of high concentration impregnation is restricted by the need to evaporate some of the water entering the system as fresh wood is quite wet. The energy economy of such a process is questionable.

The question of alkali consumption is interesting since, as seen in Figure 60, there was evidence that the methanol vapor phase process had higher yield than the water-only processes. If the extra yield was due to less carbohydrate peeling, this should also be seen as lower alkali consumption, as alkali is consumed in carbohydrate degrading reactions. In Figure 69 the alkali consumption for methanol vapor phase, water steam phase and batch kraft pulping are presented as a function of lignin yield when using constant end of cook alkalinity.

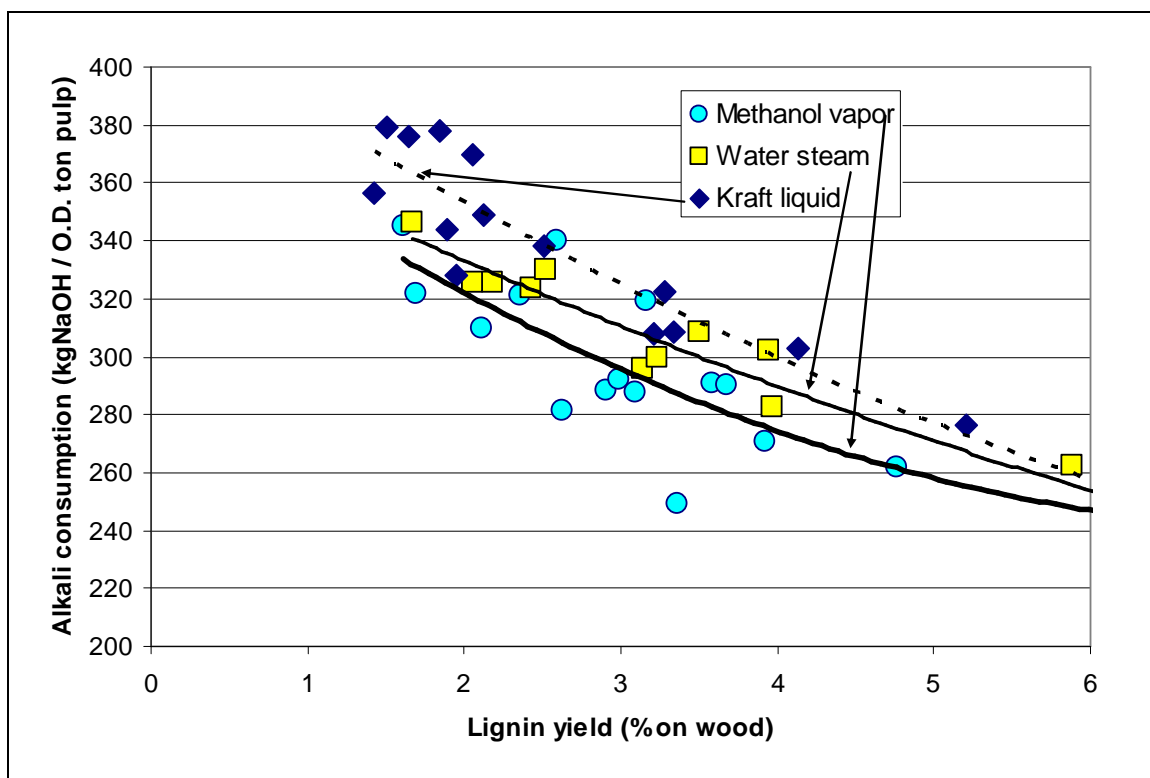
The wide variation in the results is due to the fact that the experimental procedure was not very well suited to study alkali balances. The washing out of residual alkali from cooked chips leads to a certain uncertainty which is particularly evident in vapor phase pulping. Also, the amount of liquor in the pipes and valves of the equipment can never be known with 100% accuracy. Taking into account the additional uncertainty related to the

procedures for titrating low concentrations of alkali from liquors containing large amounts of dissolved organic salts, it is clear that the current research will only give an estimate of consumption, while exact figures require larger scale tests.



**Figure 69. Alkali consumption vs. lignin yield for various cooking methods, constant end-of-cook alkalinity.**

The question of alkali consumption is worth returning to one more time. As the actual purpose of kraft pulping is to produce as much papermaking pulp as possible from a given amount of wood using as little chemicals as possible, it is felt that any comparison of different cooking methods should be made as a function of the pulp produced. Such a comparison is shown in Figure 70.

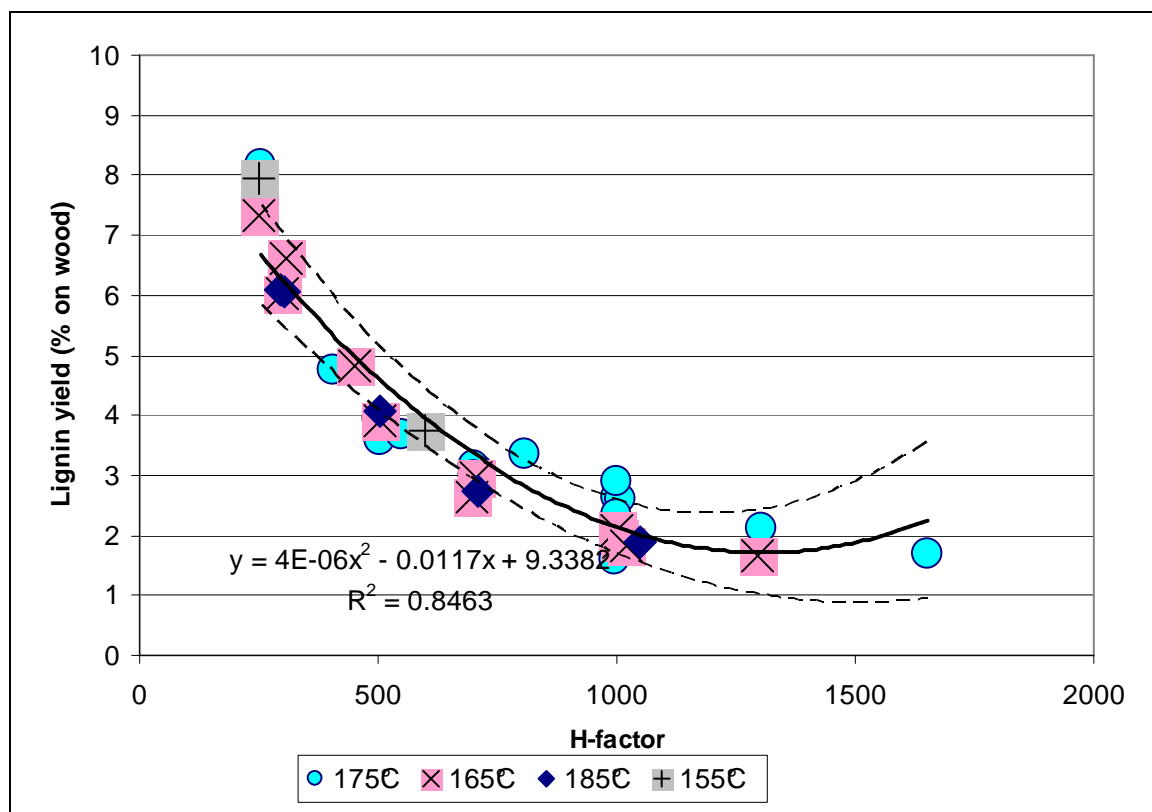


**Figure 70. Alkali consumption vs. lignin yield as a function of the amount of pulp produced using the various pulping methods, 80°C im pregation, constant end-of-cook alkalinity.**

Based on Figure 70, it seems that the yield benefit of methanol vapor phase pulping also can be seen as a reduced need for alkali. As before, there is quite high variability in the experiments, so the consumption figures should be verified in larger-scale experiments.

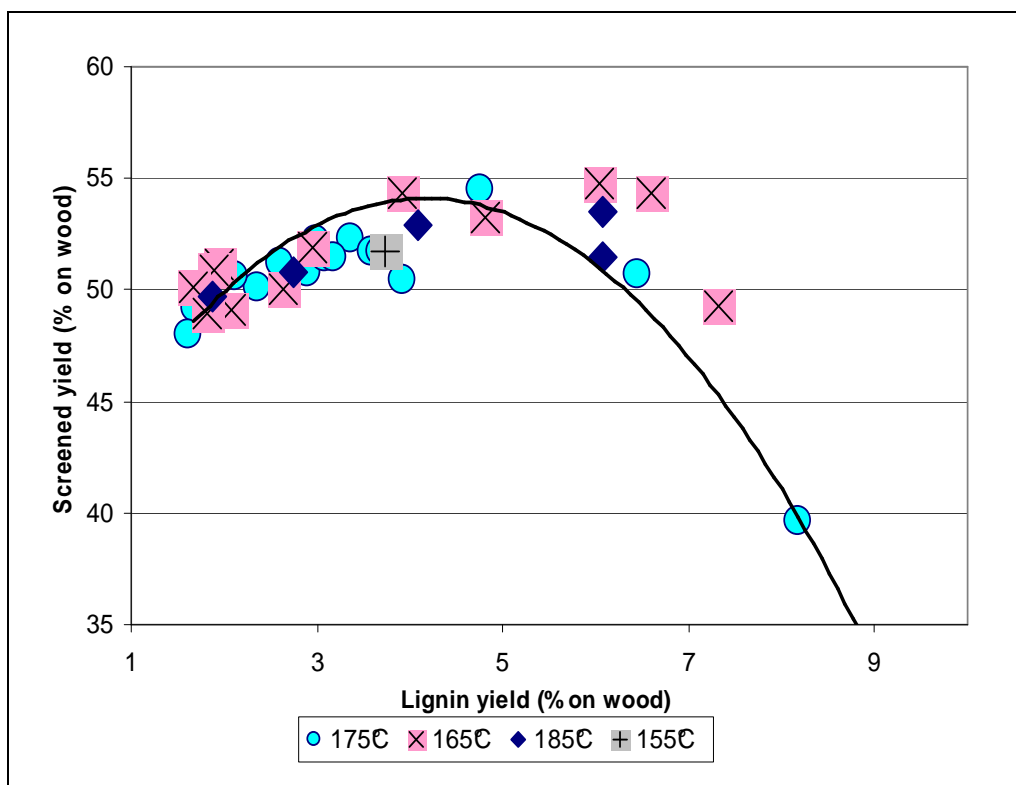
#### **4.5.5 Impact of cooking temperature in methanol vapor phase pulping**

175°C had been chosen as the main cooking temperature in the experiments, as explained in section 3.2. After the cooking method had been established, it was of interest to study the effect of temperature on delignification.



**Figure 71. Achievable lignin yield vs. H-factor in methanol vapor phase pulping at 155, 165, 175 and 185°C.**

Figure 71 shows that the pattern of delignification in methanol vapor phase pulping is much the same as in conventional kraft pulping, as far as the time-temperature behavior is concerned. A 10°C increase in temperature doubles the pulping speed, just as the H-factor model predicts. This result can be seen as further evidence that methanol does not change the actual pulping chemistry but merely works as a “booster” for cooking speed.



The limited impact of cooking temperature on the outcome in pulping is further supported by Figure 73, the rejects levels do not change significantly over the lignin yield range studied when using methanol vapor phase pulping.

## 4.6 Tests to chart the impact of methanol

To gain a better understanding of the effect of methanol on kraft pulping, the main path of cooking experiments was abandoned in favor of testing the impact of methanol on sub-processes. The first sub-process to be tested was the impact of alcohol on the penetration of cooking liquor into the wood. It was argued that a change in for instance surface tension of the impregnating liquor due to alcohol addition could lead to more efficient impregnation. To clarify the situation, a study was conducted using the impregnation equipment at HUT. Studies were also performed to clarify the impact of the increased digester pressure associated with the use of alcohols on pulping and also the impact of using solvents other than methanol.

### 4.6.1 Methanol in penetration

The results in Figure 74 show how penetration of the heartwood chips proceeds at 25°C with pure water, a mixture of water and mill white liquor, and a mixture of water, methanol and mill white liquor. The temperature 25°C has been depicted, as the differences are clearest at low temperature. The same impact of methanol addition was also seen at higher temperature and at all impregnation pressures used. Tests with all liquors were performed using 1-, 5- and 9-bar overpressure and at 25 and 70°C.

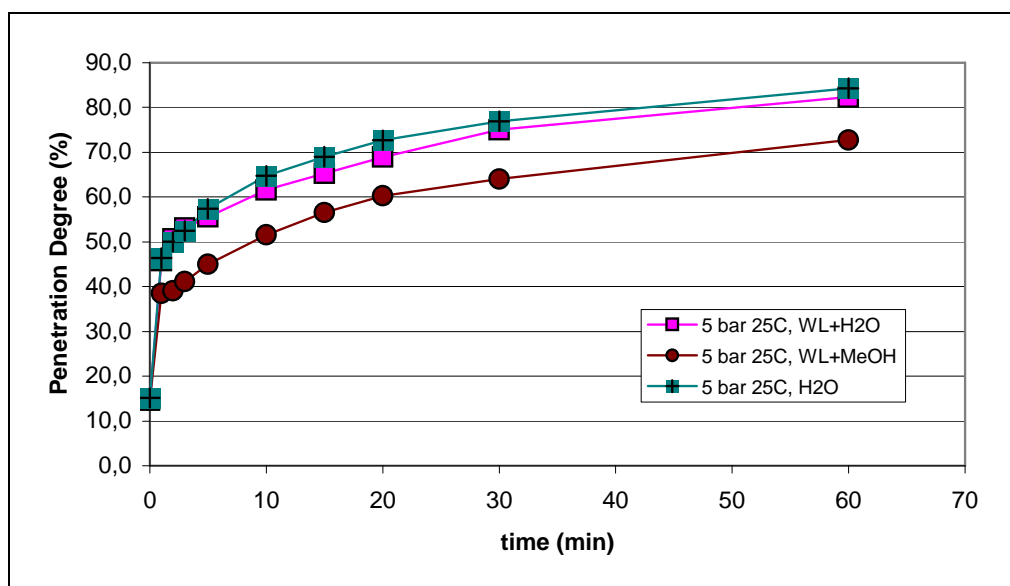


Figure 74. Degree of penetration vs. time for impregnation liquors with and without methanol addition.

The chip penetration with liquor containing methanol was clearly slower than of that without methanol, showing that the benefit seen from the use of methanol was not due to improved penetration. This observation is in agreement with the earlier results, i.e. that an



addition of methanol does not reduce the rejects content in batch pulping without liquor exchange.

#### 4.6.2 Tests to chart the impact of increased digester pressure in cooking

The addition of methanol also increases the digester pressure due to the high vapor pressure of methanol compared to water. High pressure early in the cook is known to be beneficial if impregnation is inadequate. The effect of high pressure pulping was tested in a series of experiments with high digester pressure applied at the beginning of heat-up in normal batch kraft pulping. The tests had to be performed without methanol to be able to isolate the effect of increased digester pressure. This study was performed using the same chips as in the impregnation study, i.e. chips from Malkov's thesis study. The use of geometrically regular chips ensured that the results were comparable, as any irregularity of the chips would influence the penetration behavior of the chips. The chips had the added benefit that heart- and sapwood had been kept separate, so the effect on both types of wood could be studied separately.

Two series of cooking with the push-pull digester tests were performed, the first with minimal impregnation as seen in Table 15. Heartwood and sapwood chips were cooked separately. All cooks were essentially identical except that in the cooks indicated by p25 the digester pressure was increased to 25 bar by adding nitrogen. The experimental set-up was the same as in the liquid phase batch cooks described earlier. The pressure in methanol pulping at 175°C is around 13 bar, so if higher digester pressure is beneficial, the chosen conditions should give clear indication. In the first cooking series with minimal impregnation, the impact of high pressure in the cooking stage on rejects is rather big, especially for heartwood (Table 16).

**Table 15. Cooking conditions in pressure test cooks with short impregnation**

<b>Impregnation time (min.)</b>	<b>Heat-up time (min.)</b>	<b>H-factor</b>	<b>Cooking temperature</b>	<b>Alkali charge (% EA on wood)</b>
5	5	1500	175°C	19.3

**Table 16. Cooking results for pressure test cooks with short impregnation**

<b>Wood type</b>	<b>Digester pressure</b>	<b>Kappa no.</b>	<b>Yield (% on wood)</b>	<b>Rejects (% on wood)</b>
Heartwood	normal	59.9	54.0	5.8
Heartwood	25 bars	60.5	53.8	3.1
Sapwood	normal	68.0	56.3	13.0
Sapwood	25 bars	65.0	55.0	11.5

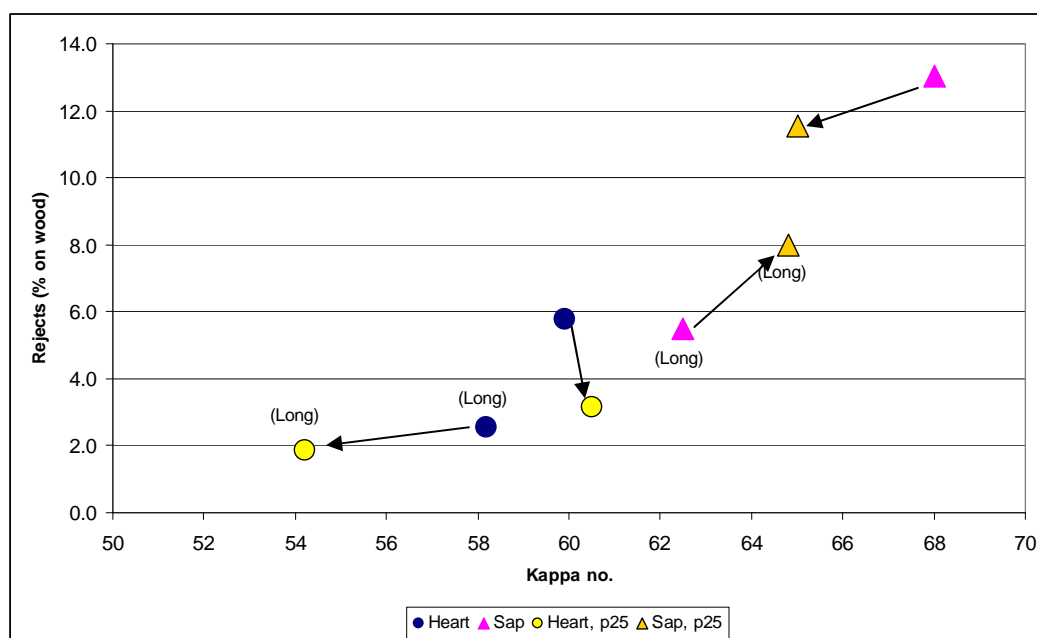
In the second series of tests the impregnation was prolonged before heat-up and the application of high pressure as presented in Table 17. The effect of these experiments can be seen in Table 18. A longer impregnation time has a clear impact on both kappa number and rejects levels but the effect of pressure becomes hard to identify. In fact, the impact of impregnation seems to be more clear-cut than the effect of the additional pressure applied.

**Table 17. Cooking conditions in long impregnation pressure test cooks**

Impregnation time (min.)	Heat-up time (min.)	H-factor	Cooking temperature	Alkali charge (% EA on wood)
60	5	1500	175°C	19.3

**Table 18. Cooking results for long impregnation pressure test cooks**

Wood type	Digester pressure	Kappa no.	Yield (% on wood)	Rejects (% on wood)
Heartwood	normal	58.2	52.4	2.6
Heartwood	25 bars	54.2	52.4	1.8
Sapwood	normal	62.5	54.3	5.5
Sapwood	25 bars	64.8	54.8	8.0

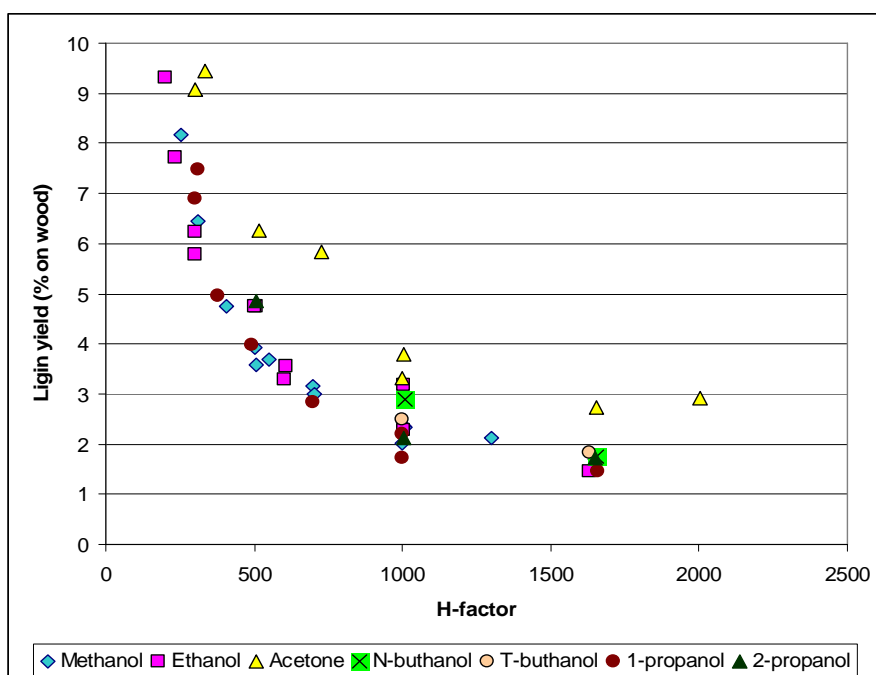


**Figure 75. Rejects vs. kappa number for heart- and sapwood cooks at normal and elevated digester pressure (25 bar =p25) using long or short impregnation. Arrows show results for corresponding cooks going from low to high pressure.**

The high kappa number range in the experiments was chosen in order to make sure that all cooks produced measurable rejects levels, as the idea of the experiments was to compare the level of rejects and the level of delignification achieved. As can be seen from Figure 75, the incremental benefit from high pressure pulping was not very big in the cooks where impregnation was sufficient. Especially for easily penetrated sapwood the effect is within the limits of the experimental accuracy. The arrows in Figure 75 showing the move from low to high pressure would be expected to point to the lower left corner of the picture if the change in delignification behavior would be due to pressure. The results are not very conclusive.

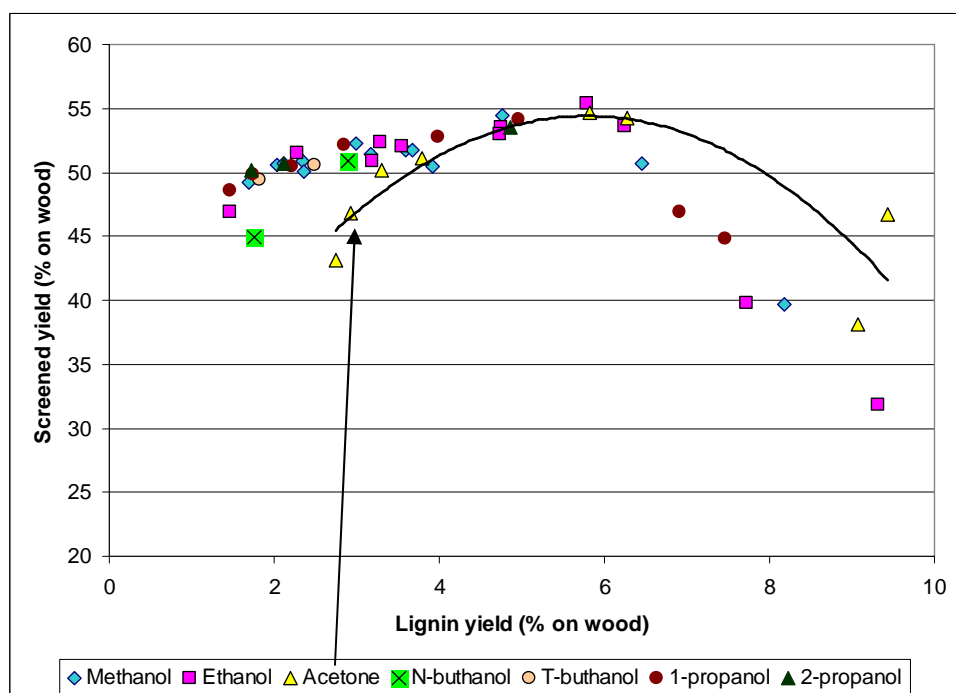
### 4.6.3 Tests with organic solvents other than methanol

Having established the fact that methanol vapor phase pulping is possible and quite beneficial, it was of interest to study whether the effects seen were methanol-specific. In order to do this, several other solvents were also tested. The solvents tested included 1- & 2-Propanol, Ethanol, N- & T-Buthanol and Acetone. The experimental setup was identical to that used for methanol vapor and water steam phase cooking, impregnation followed by liquor withdrawal and heating using a minimal quantity of the solvent under study. The results are shown in the following figures.



**Figure 76. Lignin yield vs. H-factor for softwood using various solvents in vapor phase pulping.**

As is evident from Figure 76, the kinetic benefit of all solvents except acetone is similar to that of methanol. This is quite an interesting results when considering the range of molar weights and other properties involved. It is almost as if the important thing is to remove the water from the system and not so much what solvent is used. An interesting question is what the effect of acetone is. Pulping is slower than with the other solvents, but clearly there is still delignification taking place. It is as if the level of delignification achievable with acetone would be inferior to that achieved with other solvents, even when there is still some residual alkali left that should make continued delignification possible.



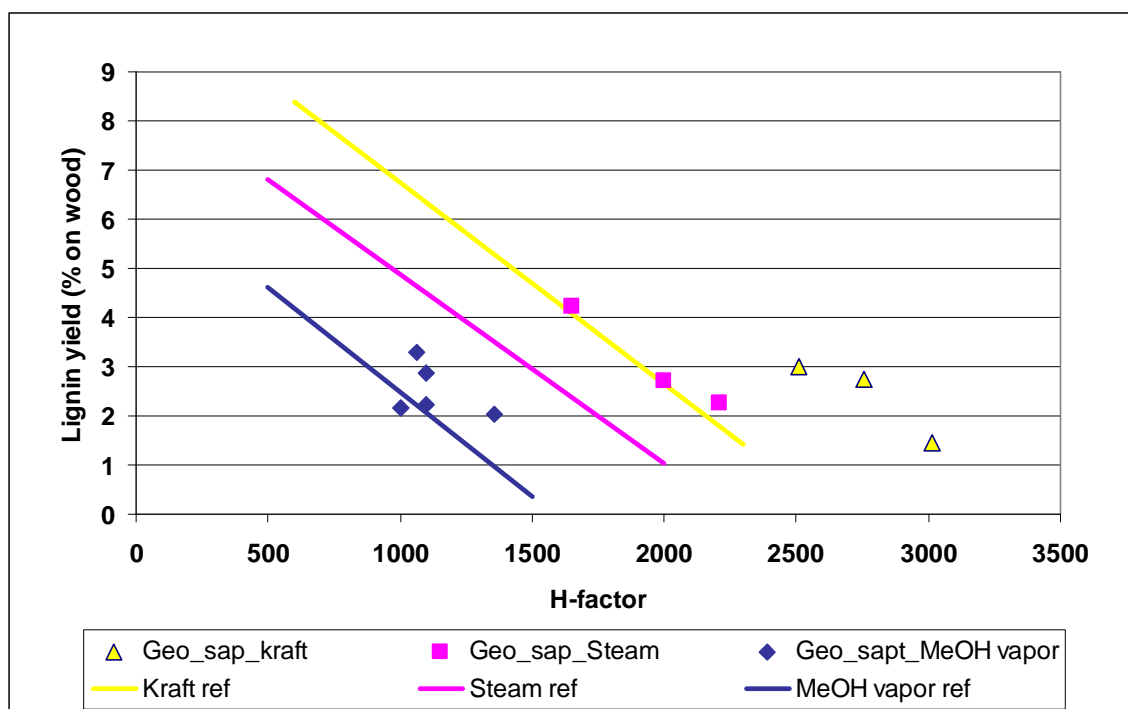
**Figure 77. Screened yield vs. lignin yield for softwood using various solvents in vapor phase pulping.**

As seen in Figure 77, the screened yield of the various solvent vapor phase pulping methods behaves much like that of methanol for all cases except acetone. For some reason, yield drops at low lignin yield when acetone is used as the heating medium, without the delignification going any further. The resulting pulp was also quite dark compared to the other pulps. The behavior of acetone vapor phase cooking was rather surprising although acetone is known to be quite different from the other solvents used. No further testing was done to clarify the reason for this odd behavior, but it is felt that it probably could give some clues as to the nature of the benefit produced by the addition of solvents to kraft pulping.

#### 4.6.4 Thick chips

During the course of the investigation, several theories about the reason for the benefit of methanol addition have been discussed. Many of the theories have centered on the solubility of alkali in different media. Inorganic sodium salts dissolve more easily in water than they do in organic solvents. This could be a mechanism by which the alkali would be “forced” to stay in the wood instead of becoming part of the surrounding liquor. The hypothesis was tested by the following experiment: Thick softwood chips were fabricated as explained earlier and pulped with the three different pulping methods. The idea was that with thicker chips the surface area of the chips in contact with the heating media would decrease. In case of a chemistry based explanation, this should decrease the effect of using methanol. Also, if the explanation has to do with the relative solubility of alkali in the different media, the relative difference between heating with water steam and methanol vapor could be expected to decrease, as the surface coming in contact with the heating media decreases.

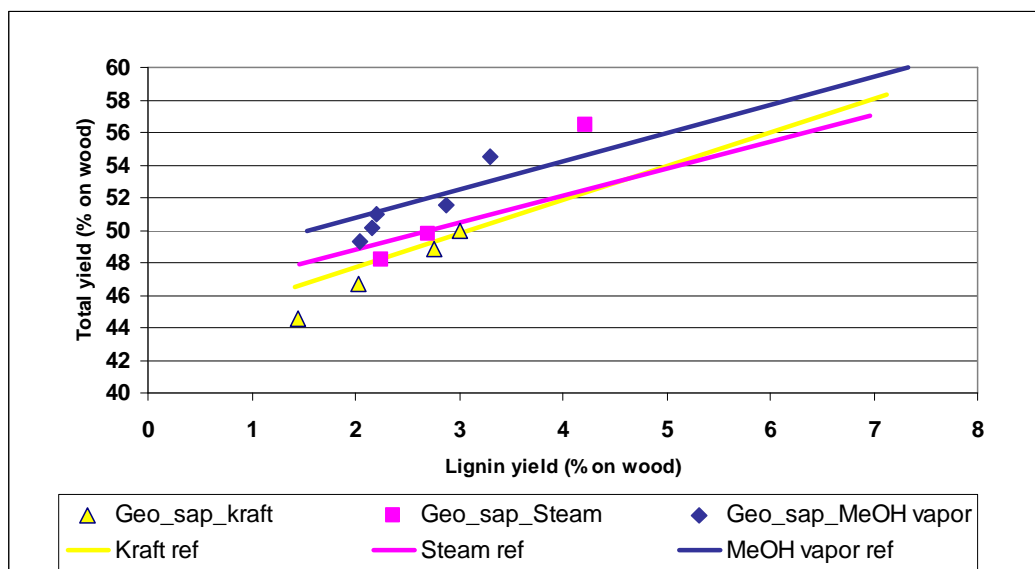
The results of the experiments with thick handmade chips are presented in the following figures. The linear trends in the figures represent the results for the various methods with normal chips.



**Figure 78. Comparison of softwood lignin yield vs. H-factor for thick geometrical sapwood chips and ordinary softwood chips (ref.) using different cooking methods. Constant end of cook alkalinity.**

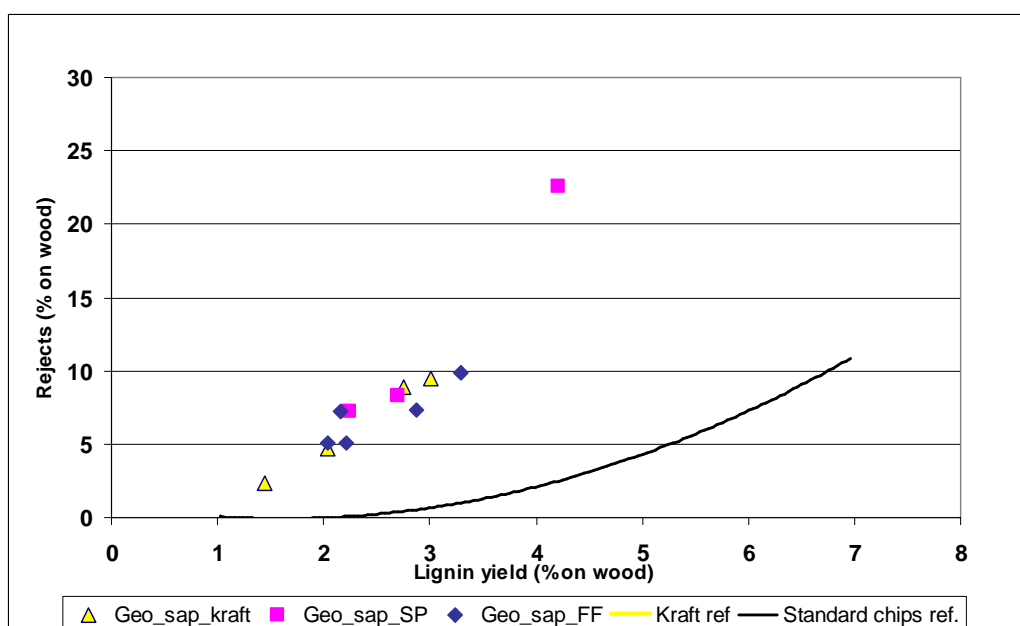
Figure 78 clearly shows that the benefit of using methanol vapor as a heating medium is still present also with thick chips. This is seen as an indication that the benefit is based on the solubility of alkali in organic solvents, the idea being that the methanol is unable to wash out the cooking chemicals from the wood during heat-up to the same extent as water steam. This finding could also be used to enable pulping of thicker chips than currently possible, something that could be used to increase process yield.

Rather surprising is, however, the big difference in delignification speed between normal and thick chips when using water steam. If the effect speeding up kraft pulping when solvent is present has to do with the solubility of alkali, the smaller surface area / volume ratio of thick chips could be expected to be beneficial also in water steam pulping.



**Figure 79. Comparison of softwood total yield vs. lignin yield for thick geometrical sapwood chips and ordinary softwood chips (ref.) using different cooking methods.**

Figure 79 shows the total yield vs. lignin yield for the geometrical chips using the different cooking methods. The yields seem quite similar to those achieved with thin chips. All cooks, however, had high rejects, so the screened yields are significantly lower. The behavior of the rejects was quite similar for all cooking methods as seen in Figure 80.



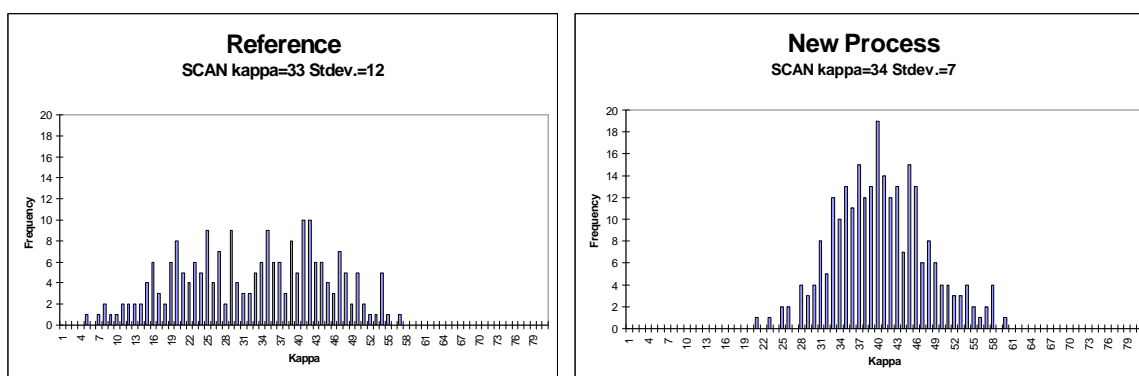
**Figure 80. Rejects vs. lignin yield for thick geometrical sapwood chips and ordinary softwood chips (ref.) using different cooking methods.**

#### 4.6.5 Uniformity of pulping

An early hypothesis regarding the effect of methanol addition was that it would somehow affect the uniformity of pulping, possibly by “forcing” the delignifying chemicals deeper into the wood due to decrease solubility. Testing the uniformity of pulp delignification

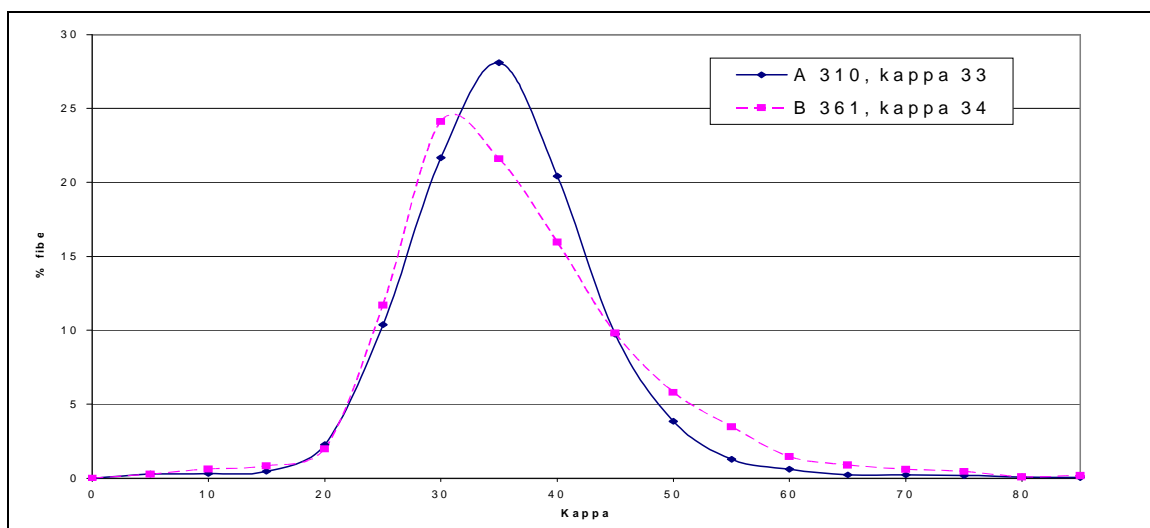
was therefore of great interest. The uniformity of pulping can be measured by fiber kappa analysis (FKA) based on fluorescence of stained lignin or by IR measurements of pulp pads. Both methods are relatively fast and simple, but also dependent on calibration using samples with known kappa numbers. For the IR measurements calibration is performed by measuring all samples in a series with known kappa numbers and then applying principal components analysis to determine the spectral compositions corresponding to different degrees of delignification. In the fiber kappa analyzer system the red/green ratio of acridine orange fluorescence is calibrated using the known samples.

In order to get as much information as possible about the delignification uniformity of the methanol vapor phase pulping method, a series of samples for both methanol vapor phase and liquid kraft pulping was tested with both methods mentioned above. The results for two pulps at the kappa number level 33-34 are shown in Figure 81 and Figure 82. The testing using IR spectroscopy was performed by personnel at the Laboratory of Wood Chemistry of HUT and the fiber kappa measurements by the staff at the University of Washington.



**Figure 81. FT-IR measured kappa distributions of liquid phase kraft cook (reference) and MeOH vapour phase cook (new process). The histograms show the distribution of kappa numbers measured for the pulp samples. 250 individual points measured/sample. Mean kappa numbers given by the FT-IR measurements 30 for kraft and 40 for MeOH vapor phase.**

For the FT-IR measurements, the kappa distribution of methanol vapor phase (new process) is much narrower than that of the reference kraft. This result supports the hypothesis that the low rejects is due to better pulping uniformity. The limited correlation between measured SCAN-kappa number and the kappa number predicted by the FT-IR measurements raises some questions.



**Figure 82. Fiber kappa analysis (FKA) kappa distributions of liquid phase kraft cook (A 310) and MeOH vapor phase cook (B 361).**

On the other hand, the FKA results from the University of Washington do not support the IR-measurement results. According to these results, the uniformity of methanol vapor phase cooking is inferior to that of kraft liquid phase pulping. An interesting feature in the FKA results is the fact that the distribution of fiber kappa numbers is less symmetrical than that of liquid phase cooking.

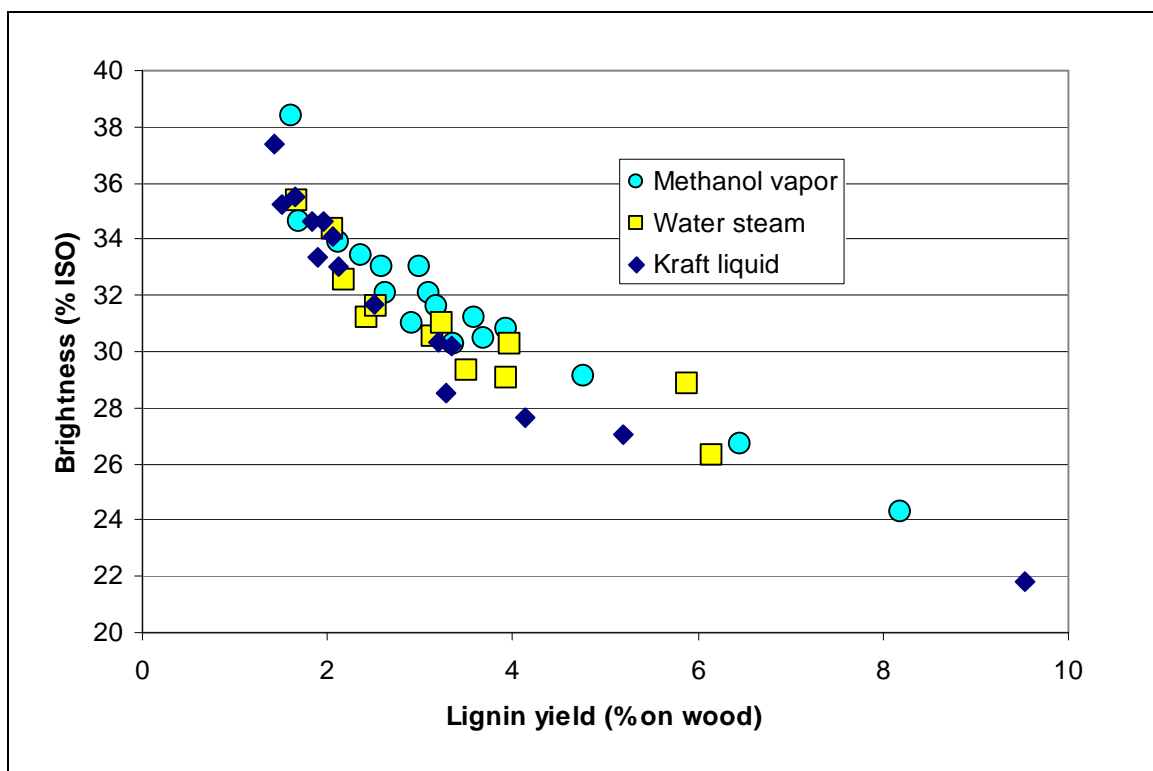
No simple reason could be found for the apparent contradiction in the results between the two measurement methods. The problem was deemed too complex to be investigated further in the present study but is clearly an interesting area for further research.

#### **4.7 Fiber properties**

The present investigation was only aimed at looking into fundamental questions regarding pulping speed under various conditions. The question of pulp quality was left outside the scope of the research. It was felt that as the active delignifying chemicals are the same as in conventional kraft pulping, the properties of the fibers would be unlikely to change to any major extent. Also, making a whole set of fiber property measurements for each incremental change in process design would have been far beyond the capabilities of the current project.

Some basic features of the resulting pulps were, however, measured. The results of these measurements are presented below.

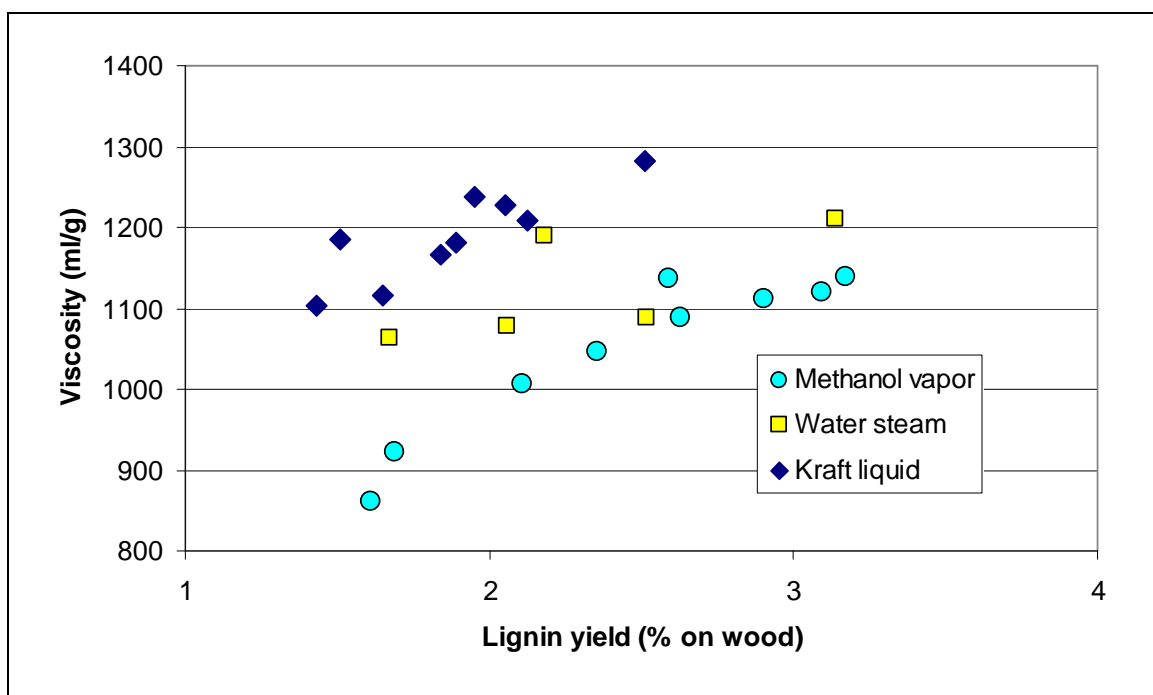




**Figure 83. Brightness vs. lignin yield for the cooking methods under study.**

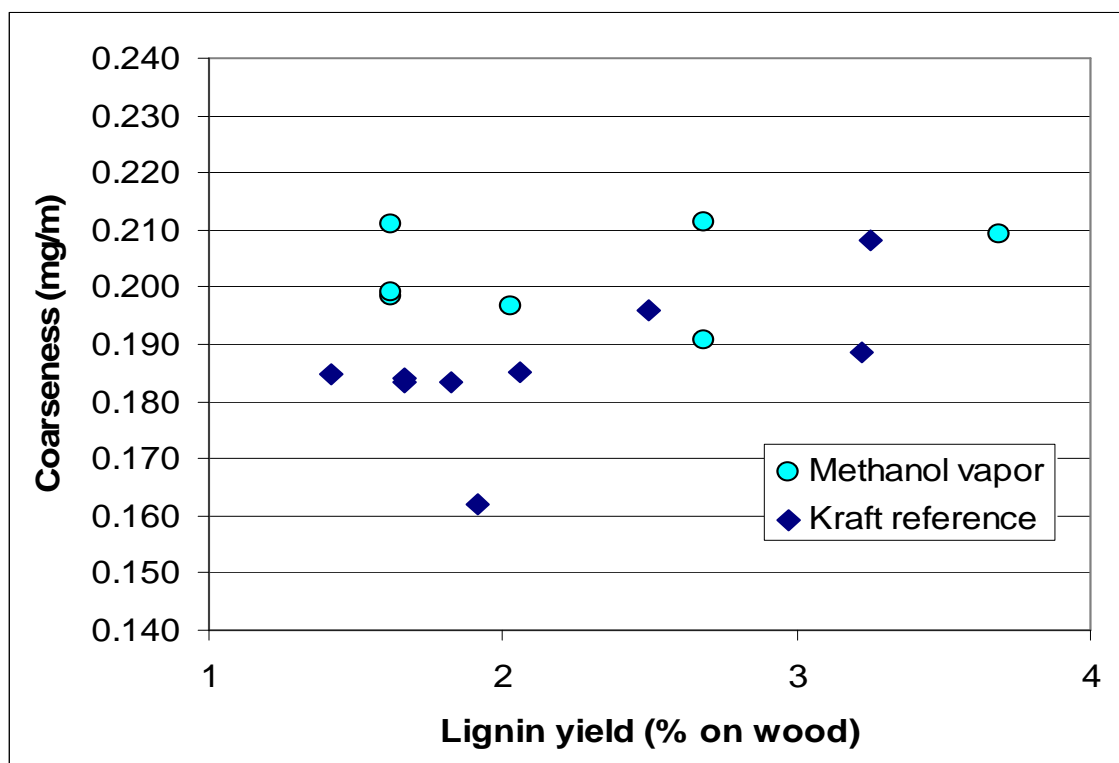
As seen in Figure 83, there is a slight brightness advantage for the methanol pulping method compared to the two other ones.

Viscosity vs. delignification is shown in Figure 84. The current investigation did not see the maximization of pulp viscosity as an aim, but as so much literature centers around pulp viscosity it was felt that this parameter needed to be presented.



**Figure 84. Viscosity vs. lignin yield for the cooking methods under study.**

Clearly, the viscosity of methanol vapor phase pulping is lower than that of the other pulping methods. The fact that the viscosity of methanol vapor phase pulps is lower than that of water steam phase pulps indicates that it is not only the high concentration in impregnation that is responsible for the drop as the concentrations are similar in both pulping methods. A factor may be the high hemicellulose content that increases the proportion of lower molecular mass molecules in the pulp.



**Figure 85. Fiber coarseness vs. lignin yield for methanol vapor phase pulping and liquid phase kraft pulping.**

Fiber coarseness was measured from the same pulps that were used in the delignification uniformity studies. The results are more reliable at lower lignin yields, as there was a tendency of clogging in the equipment when measuring less delignified pulps. From Figure 85 it can be seen that the superior yield of the methanol vapor phase cooking can be seen as a higher fiber coarseness when compared to conventional liquid phase kraft pulping.

## 5 Discussion

The PuPu digester system enabled work in a parameter range never studied before. The equipment is unique in its ability to allow fast heating up and gave new possibilities to study the basic interactions in kraft pulping. It also allowed studying the impact of organic solvents on these interactions. The study was based on short series of experiments whose results were evaluated and used as a basis for the next experimental setup. However, the central theme of the research was to find methods to reduce the overall process time as much as possible.

As is illustrated by the review of laboratory equipment in section 2.5, the present investigation would not have been possible without the new digester.

### **5.1 Impregnation and heat-up**

One of the key features of the PuPu digester system was that it enabled the use of very short heat-up times. This made it possible for the first time to study the impact of heat-up time on identical cooks over a range from 3 minutes to 90 minutes.

Figure 44 and Figure 45 show that the heat-up time has no impact on the extent of delignification or yield at this level of delignification. In terms of intensification this means that there is no lower limit for how fast heat-up can be performed from the point of view of delignification. According to the further results in section 4.1, the only barrier to reducing impregnation and heat-up times is the formation of rejects, i.e. pulping non-uniformity. A very short heat-up time lowers the threshold for rejects formation. The absolute level of this threshold is governed by chip properties and pre-treatment such as steaming. It must be remembered, that in this investigation the chips were thin and well steamed prior to the experiments.

The results are very significant as no published research has been found where the heat-up time has been varied over such a broad range using the same chip supply and digester. Modern industrial systems, such as hot liquor displacement and steam phase top digesters, use very rapid heating. According to current results, this does not have any negative impacts on the pulp. This fact has not been measured before. The data that exist from earlier refer to cooks without steaming and thus proper impregnation as seen in section 2.2.1. The results in Figure 51 clearly contradict the results found in the literature presented in Figure 9. The reason for the difference is that the results in the literature refer to cooks without proper impregnation.

To further shorten the overall process time, the effect of the combination of impregnation and heat-up time was studied. According to the results in Figure 46 and Figure 47, the impregnation time can be brought down to 5 minutes and heat-up can be performed as fast as possible without any detrimental impact on the pulping results seen as yield and pulping speed when delignification is taken to a normal industrial level. Possible changes in fiber level delignification uniformity were not studied at this point. The lower limit for impregnation and heat-up time is determined by the uniformity of cooking as seen in Figure 48. If a normal kraft cook is intensified as much as possible, there is a tendency towards higher rejects at high lignin content levels. In this context it is important to remember that the chips used in the current study were thinner than normal mill chips, meaning that the absolute lignin yield level giving significant rejects probably is lower with “normal” chips. Also, it has to be remembered that laboratory screening is not the same as mill screening with pressure screens. The fact that there seems to be very little difference in rejects between cooks with 5 and 60 minutes’ impregnation is noteworthy. It implies that impregnation at typical kraft pulping alkali concentrations has a rather small impact on rejects. It seems that low rejects at high lignin content can only be ensured by slow heat-up in this type of cook.

From the point of view of intensification this means that it would be possible to use a very short impregnation time as long as steaming has been performed well and delignification is taken far enough. However, in the present work, the aim was not to

shorten the impregnation time. This is because impregnation can be performed below 100°C and therefore does not require the use of pressure vessels. As the stated aim of the present investigation was to decrease the size of the pressure vessel, the question of impregnation time was not investigated further. However, the fact that the heat-up time can be kept short is good news as far as process intensification is concerned.

## **5.2 Impact of methanol addition**

The second step in the experimental investigation was to test the effect of methanol addition on kraft pulping. The results in Figure 49 clearly show the impact of adding 50% methanol to the cooking liquor. The degree of delignification as indicated by the lignin yield dropped by 30% from 1.5 to 1, regardless of heat-up time. This result is in agreement with earlier studies that also show a clear favorable effect on delignification from the addition of alcohol, as explained in section 2.4.3. Because experimental setups used by different researchers vary significantly, it is hard to compare absolute numbers, but the levels seem similar. The fact that Figure 50 shows a slight decrease in total yield for the methanol-containing cooks is understandable, as the delignification has progressed further in these cooks.

Figure 51 shows that the viscosity of the pulps from methanol-containing cooks tends to be lower than that of conventional kraft cooks. This can be due to the greater delignification achieved in these cooks.

Looking at Figure 53, Figure 54 and Figure 55, two things are evident. Firstly, just as for non-methanol cooking, impregnation and heat-up time can be shortened at will for methanol-containing cooks without adversely impacting the results for yield and degree of delignification. This is proven by the fact that all results fit into the 95% confidence intervals. Secondly, methanol works as an intensifier of the kraft process over the whole delignification range. The delignification time as given by the H-factor drops 30-50% over the whole delignification range. Other researchers have reported drops in kappa number at constant cooking times, but few have investigated the effect of a wide range of delignification degrees, as performed in the current investigation. Many of the earlier studies have been aimed at reducing sulfidity, so the kinetic benefit of alcohol addition has been used up as a reduction of sulfur without needing a longer cooking time.

When comparing total yield over a wider range of delignification, as shown in Figure 53, a clear benefit of using alcohol in delignification can be seen. The total yield of the methanol-containing cooks is around 2 percentage points higher than that of the conventional kraft cooks across the scale of delignification degrees. This concurs with the results of Norman et al. /97, 101/.

Screened yield is also improved in the technically interesting kappa number range of 20-30, as is seen in Figure 55. Again, it must be stressed that the laboratory screened yield is not in clear correlation with industrial screened yield. The advantage in screened yield is lost at higher lignin content due to higher rejects content. It is understandable that the very short high-lignin-content cooks using methanol will give high rejects, as the overall process time is extremely short.

### **5.3 Impact of the allocation of methanol addition**

To further study the effect of methanol on kraft pulping, additional cooking experiments were performed. Figure 56 shows that the benefit for pulping speed of the addition of methanol is independent of whether the alcohol is added during impregnation or used as a displacement heating agent. This is a remarkable result.

The result shows that methanol can not be an active delignifying chemical as it is clear that the methanol can not have time to diffuse into the chip when it is added only as a heating medium after impregnation. Compared for instance to the HO<sup>-</sup> and HS<sup>-</sup> ions, which are dependent on being impregnated into the wood to be effective, the difference is clear. It is also unlikely that the effect of methanol would be to help dissolve the lignin from the wood, as saturating the wood structure with methanol should also show up as faster cooking. This is an aspect of solvent pulping that has not been reported earlier.

When comparing the screened yields of the two methods of methanol enhanced cooking, a clear advantage is seen for so called methanol cooking (Figure 57). The high screened yield in displacement pulping comes from a combination of high total yield and low rejects. The low rejects are probably in part due to the fact that a stronger impregnation liquor has to be employed in a cook with displacement heating, as the alkali otherwise would be depleted in the cooking step. The use of strong impregnation liquor brings a clear improvement in impregnation, as seen in the results of Hultholm et al. shown in Figure 19. The benefit for rejects is of the same type as shown in Figure 24 for white liquor impregnation pulping. The benefit in total yield compared to conventional kraft pulping is partly explained by the impregnation characteristics and thus more uniform pulping, but also by the impact of methanol.

When the amount of methanol in the reaction phase was reduced and vapor phase pulping was tried, it was found that the reaction time was reduced further, especially for higher lignin content pulps (Figure 59). Methanol vapor phase pulping is clearly faster than methanol liquid phase pulping. This indicates that the effect of methanol on delignification can not be one of lignin dissolution into organic solvents, because then a larger volume of solvent should be beneficial. Instead, it seems that the solubility of inorganic chemicals could hold the answer to the increased speed for methanol enhanced pulping.

The results for water steam phase pulping confirm that there is a benefit for pulping speed in adopting a lower liquor-to-wood ratio in the cooking stage. The cooking speed of water steam phase pulping is very close to that of liquid phase methanol pulping and clearly faster than that of liquid phase kraft corresponding to the steam phase pulping research by other researchers.

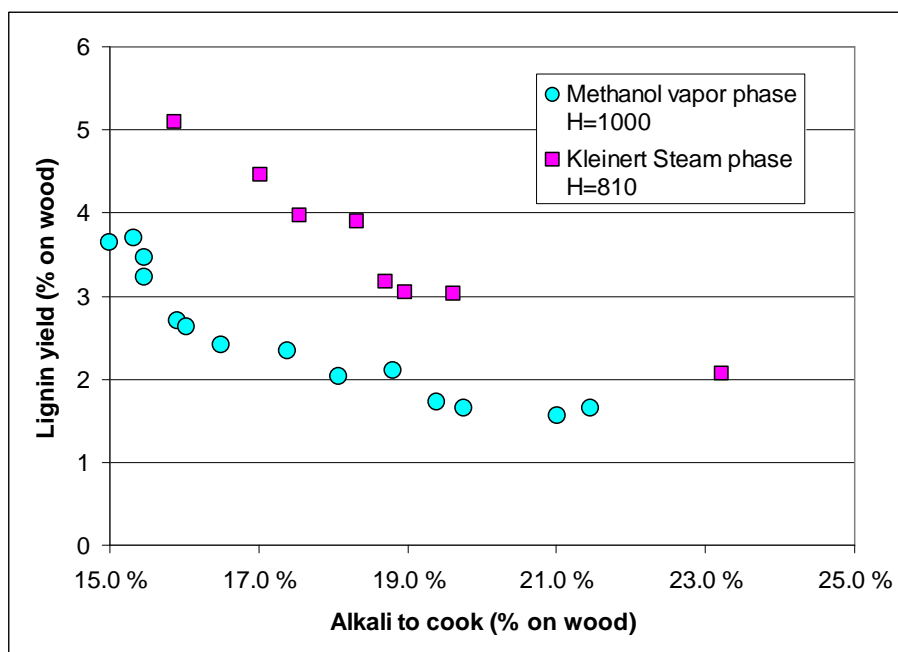
Figure 60 shows that the yield benefit for methanol aided pulping is achieved also in vapor phase pulping. A yield benefit for water steam phase pulping over liquid phase kraft can also be seen, as was shown by Kleinert and Ahlgren & Olausson /10, 59/. Methanol vapor phase pulping has not been reported earlier. The high yield of steam phase pulping is in conflict with the rules of modified pulping that are supposed to decrease carbohydrate degradation and thereby give higher pulp yield. The high yield in vapor phase pulping is, however, undisputable.

The fact that vapor phase pulping is possible using methanol as the heating medium is a novel finding. It gives clear benefits over both water steam phase pulping and methanol liquid phase pulping. This invention was patented /122/.

#### 5.4 Effect of impregnation on methanol vapor phase pulping – the alkali to cook concept

In vapor phase pulping, where all mass transfer must happen prior to heat-up, impregnation concentration, impregnation time and impregnation temperature can be combined into a single parameter, called alkali to cook. This parameter can be used as a way of estimating the impact of impregnation on the maximum achievable level of delignification in the cooking stage. The same basic idea was used by Kleinert, as seen in Figure 20. He used the term alkali charge to describe the amount of alkali transferred to the cooking stage.

In Figure 86 the results for methanol vapor phase pulping to H-factor 1000 are compared to Kleinert's research. In this comparison the methanol cooks have a longer cooking time (H=1000 vs. 810), but as was seen in Figure 66, it is the amount of alkali that plays the biggest role for the extent of delignification at least to around 17% alkali to cook. This is illustrated by the linear trend followed by the results up to that point in Figure 66. Also, cook number 542, used to construct Figure 67, with an alkali to cook of 20.6% reached a lignin yield of 2.3 % on wood after only 700 H-factors. Clearly, cooking time is not the only explanation for the difference, the use of methanol also plays a role.



**Figure 86. Results for methanol vapor phase cooking from present research compared to data for Kleinert's research with water steam phase pulping. Constant cooking times in both series.**

The results in the present investigation and those of Kleinert are very similar. A step change in the level of delignification achievable is clearly seen. Whether this is due to

only to the presence of methanol in the present investigation or if chip properties play a role is impossible to say, but the difference resembles that seen in Figure 67.

An unexpected result is that lignin free screened yield does not decrease with decreasing lignin yield in the range of 4-2% lignin on wood as seen in Figure 65. This is a further contradiction of earlier claims that high alkali charges lead to yield loss. In vapor phase pulping, this clearly is not the case.

The use of constant cooking time, as was done in the research on alkali to cook, is not in agreement with the constant end-of-cook alkalinity methodology employed in the rest of the research. The use of constant cooking time, however, illustrates the impact of available alkali in a clear manner. In a mill situation, the amount of chemicals used will be minimized to avoid putting a strain on the chemical recovery system.

### **5.5 Diffusion restriction in kraft pulping**

Figure 67 shows the impact of impregnation on pulping speed. Clearly, having the needed chemicals inside the wood matrix at the onset of cooking reactions can decrease the cooking time by over 20% in conventional kraft pulping, assuming a total alkali amount of 20% EA as NaOH on wood. What makes this result remarkable is that as the same amount of chemicals is used in all of the experiments, the difference must come from the time needed to transfer the chemicals into the wood matrix. This indicates that conventional kraft pulping is mass transfer limited in the sense that the same amount of chemicals would give a faster cook if they only were in the right place at the onset of reactions. This is true even when using thin chips as was the case in the present investigation. The result also indicates that the often used assumption in studies on kraft pulping kinetics that the concentration inside the wood chips is in straight correlation to the concentration of the surrounding liquor is highly suspect. If that was the case then the cooks with minimal impregnation should be the fastest as the concentration in the surrounding liquor is the highest in those (all chemicals are in the surrounding liquor as nothing has been impregnated). Clearly this is not the case.

The use of methanol further reduces the cooking time by 30%. The similar behavior of the two methods is striking; the lines are parallel over the whole range studied. It can also be seen that liquid phase and vapor phase cooks behave in the same manner; it is only the impregnation that really determines the speed of cooking.

### **5.6 Alkali consumption**

The cooks with constant cooking time showed a linear relationship between alkali consumption and lignin yield as seen in Figure 68. In cooks with constant end-of-cook alkalinity a trend is harder to identify (Figure 69). This is partly due to the equipment used and the inherent variation in results for black liquor alkali titration. Also, the fact that a rather broad band of end-of-cook alkalinity was accepted (5-10 g/l at pH 11) increases the variability.

If alkali consumption is viewed as a function of pulp production, the high yield of the methanol vapor phase process is seen as lower alkali consumption, as illustrated in Figure 70. Another question is the fate of the residual alkali in the black liquor. It can be argued that the residual can be reused in liquid phase cooks that typically have black liquor

impregnation as a process step, whereas vapor phase pulping must have a very high concentration in impregnation making black liquor impregnation impractical. This blurs the picture of consumption further.

### **5.7 Impact of cooking temperature**

The basic H-factor relationship between time and temperature in pulping can be used to estimate the achievable level of delignification in experiments with varying cooking time, as seen in Figure 71. The cooking temperature did not have an impact on pulp yield or rejects in the studied range. From the point of view of process intensification, this means that high temperatures can be used to shorten the process time. What temperature actually is used has to be decided based on the process steam available and considerations of total mill energy efficiency.

Figure 71 shows that an H-factor of 1000 is needed to reach a lignin yield of 2% on wood at moderate end-of-cook alkali levels. At 175°C with 5 minutes' heat-up this corresponds to a cooking time of 45 minutes. At 165°C it corresponds to 97 minutes' and at 185°C to only 19 minutes' cooking time. The impact on the digester volume needed is of course in direct relation to the cooking time.

### **5.8 Tests aimed at explaining the effect of methanol**

The aim of the current research was only to find ways to intensify kraft pulping. Scientific curiosity, however, drove the research to look for clues to the reason for superior pulping results in the presence of methanol.

#### **5.8.1 Effect of methanol on pulping physics**

Figure 74 disputes the hypothesis presented by Leduc et al. /70/, i.e. that the positive impact of organic solvents on alkaline pulping would be due to improved penetration. As far as penetration in impregnation goes, the penetration speed is clearly decreased by the addition of methanol. Based on the work by Malkov, the high viscosity of the methanol-containing liquors is likely to hinder penetration. The fact that the viscosities are higher can be seen in Figure 31, showing the viscosity of a water-alcohol mixture. The fact that methanol decreases the rate of penetration also discredits the claim by Marton & Granzow that improved cooking in the presence of alcohols would be due to better impregnation thanks to the reduced surface tension of the liquor /82/. It can be questioned how much of an impact increased penetration would have had in their research, as the heat-up time was fairly long at 30 minutes.

The effect of the increased liquor viscosity on diffusion is less clear. On the one hand, the Stokes-Einstein equation implies that an increase in liquid viscosity decreases diffusion speed. On the other hand, the glass transition point of the wood matrix may be decreased by the addition of methanol, as seen for silicone in the work by Wu et al. and Khang & Lee /112,113/, thus improving diffusion in the wood matrix.

The second hypothesis that could be ruled out was that the increased speed of delignification would be due to improved penetration thanks to the high pressure in the digester during methanol enhanced pulping. As can be seen from Table 16 and Table 18,



there was a slight positive impact on heartwood rejects from pulping using high digester pressure, but the impact on sapwood rejects was inconclusive and the effect on the extent of delignification was within the margins of experimental error for both types of wood. The fact that the benefit of methanol addition was not due to increased penetration could also be expected based on the results by Malkov et al. /26/, as they showed that the benefit for delignification of an optimized front-end treatment is only about 5-10%, not the 30% seen from methanol addition. Based on the present experiments, the effect of alcohols on kraft pulping is probably related to the pulping chemistry or an alteration of the physicochemical balance of the system. The hypothesis that the front end of the cook would be positively changed in terms of liquid penetration could be rejected based on these findings.

### **5.8.2 Effect of solvent used**

The follow-up investigation into the effect of various types of solvent showed that the effect of the alcohols used was very similar in terms of pulping speed (Figure 76). The only exception was acetone which behaved quite distinctly. Delignification using acetone stopped at a rather high lignin content and could not be taken further without significant loss of carbohydrates (Figure 77). The behavior of acetone pulping may merely be due to the fact that acetone is more aggressive towards wood than the other chemicals. The fact that it behaves very much like the other solvents at high lignin content might be a sign that there are two effects taking place at once. One would be an “organic solvent effect” perhaps connected to solubility of alkali in the heating media, working much like the effect for the other solvents. The other effect would be an acetone specific effect that kicks in at longer cooking times, when the acetone actually has diffused into the wood matrix.

### **5.8.3 Experiments using thick chips**

In further trials examining the nature of the methanol benefit, thick chips were pulped as described in the experimental section. In Figure 78 the degree of delignification achieved with various H-factors is compared for thick and ordinary chips using different pulping methods. The benefit of using methanol is more or less constant, whereas the water based methods are quite poor at delignifying the thick chips.

Using thick chips has two immediate effects. Firstly, the diffusion path for the pulping chemicals becomes longer. This means that diffusion restricted pulping methods become slower and that there is a greater risk of non-uniformity in the form of rejects. Secondly, the surface area in contact with the heating media becomes smaller for a given sample weight. This means that any transfer of chemical agents through the chip surface during the cooking stage is reduced and the direct effect of the heating media on the wood becomes smaller.

The fact that heating with methanol vapor loses little in the way of delignification speed further supports the theory that methanol does not take part in the actual delignification but only alters the chemical environment in the digester, thereby increasing the efficiency of the delignifying chemicals. A possible explanation lies in the solubility of the delignifying chemicals in the heating media. When heating with vapor the conditions in the digester will be something of a trickling bed situation with the chips covered by a liquid film. Differences in backwards diffusion from the wood to the liquid film could

explain the differences seen between the behavior of delignification in water steam and methanol vapor when going from thin to thick chips. The crucial question then becomes whether the increased volume of solvent that condenses on the surface is enough to wash out more alkali, or if the solubility of alkali is so small as to keep the delignification chemicals inside the wood. This could be investigated further, for instance by varying the chip geometry.

The difference between vapor and liquid phase heating is schematically presented in Figure 87. The point being illustrated is how vapor condenses on the chip surface creating a liquid film. The chemicals impregnated into the wood will diffuse out to this film as long as the concentration in the chip is higher. In liquid phase cooking diffusion is always from the liquid to the chip.



**Figure 87. Schematic illustration of the liquor phase and impregnated wood liquor in vapor and liquid phase pulping. The shade of the phases is an indication of the alkali concentration in the different phases during the cooking stage.**

The result that thick chips can be delignified this rapidly using methanol vapor was an unexpected result. The fact that the rejects levels are the same with all cooking methods (thick chips give high rejects) is in line with what can be expected, and implies that the delignification profile through the chip is similar in all cases.

## **5.9 Pulp uniformity and fiber properties**

In an attempt to measure if the kinetic advantage seen in vapor phase pulping was due to more even impregnation, and thus a more even delignification profile across the chips, samples were tested for delignification uniformity using two different methods. The methods were FT-IR spectroscopy and Fiber Kappa Analysis using fluorescent probes and a flow cell. As can be seen from a comparison of Figure 81 and Figure 82, the two methods gave conflicting results. This could be due to the fact that the single fiber analysis measures deeper into the cell wall than the FT-IR method, indicating differences in topochemical behavior of the pulping methods. FKA is believed to measure the whole thickness of the fiber (40  $\mu\text{m}$ ), whereas FT-IR only measures to a depth of 0.2-2  $\mu\text{m}$ . This, combined with differences in cell wall lignin distribution for the two cooking methods, could explain the results. The reason may also be due to different lignin groups being left in the wood after cooking. For instance, the way in which the fluorescent probes react with the residual lignin to give the characteristic change in red/green fluorescence ratio is not yet understood in detail. An interesting feature of the FKA distribution is an absence of a “low kappa tail”. This is seen as a very steep slope on the left side of the curve. What it means is that very little pulp has been overcooked as the cook has been very short (the degree of delignification is determined by the cooking time and not by the availability of alkali as in conventional pulping).

In the current investigation the properties of the resulting pulps were not studied further. Instead, energies were focused on finding the parameters affecting pulping speed. Also, it was assumed that as the active chemicals are the same as in conventional kraft pulping, so the resulting pulp should be very similar. Some basic parameters for the pulps are, however, known. The brightness at a given lignin yield is higher for softwood methanol pulping than for conventional kraft pulping. This is slightly surprising, as the washing out of reaction products should be inferior in the absence of an aqueous phase. Possible reasons are that fewer chromophores have time to form during the short cooking time, or that somehow, due to the presence of methanol, the formation of chromophores is altogether reduced. In any case, the formation of chromophores has to be seen as an unwanted side reaction, and the fact that it is reduced implies that the principle of process intensification is working as expected.

As for other fiber properties, pulp viscosity is clearly lower for methanol vapor phase pulping than for the other cooking methods, as seen in Figure 84. This seems to be a combination of the fact that the high concentrations used in steam phase pulping bring down the viscosity, as seen for water steam phase pulping, and also that methanol enhanced pulping has lower viscosity than purely water based pulping. The reason for the lower viscosity may be that the higher yield in methanol vapor phase pulping leads to better hemicellulose retention, with the short chained hemicellulose in turn leading to lower average pulp viscosity. The use of viscosity as a meaningful measurement of the quality of papermaking pulp is questionable at best. The present results should also serve as a word of caution to any researcher who wants to draw parallels between higher pulp viscosity and higher process yield; the results clearly do not provide support for such a parity.

The high yield of methanol vapor phase pulping is also evident in the pulp coarseness measurements, as shown in Figure 85. It is logical that higher yield leads to higher fiber coarseness, as the retained hemicellulose has to be connected to the fibers in order not to be lost in washing. What is interesting, however, is the potential impact of the better hemicellulose retention on the papermaking properties of the pulp. If the yield advantage can be maintained through a bleaching sequence, the need for refining the fibers should decrease, because higher hemicellulose content leads to better interfiber bonding. Other researchers have claimed that pulps produced with methanol+kraft have the same properties as conventional kraft pulp [97].

### ***5.10 Speculation about the impact of solvents***

The effect of alcohols on pulping clearly needs more research. The current research shows new aspects of the effect, but falls short of being able to explain it. The biggest question is how the delignification can be faster while the hemicellulose yield at the same time is higher. If the alcohols affect the apparent concentration of the alkali, this should have a negative impact on the hemicellulose yield as hemicellulose is known to be very sensitive to alkali. On the other hand, if the effect of methanol is related to better dissolution of reaction products, the step from liquid phase methanol cooking to vapor phase should have had a negative impact on the process, whereas the effect seen was the opposite. Also, if the methanol somehow altered the reactions of lignin and the cooking chemicals, having the methanol impregnated as deeply into the chips as possible could be expected to produce a beneficial effect. That this is not the case is illustrated by both the “methanol cooking” experiments and the cooks with thick chips.

The present results support the hypothesis that the effect of solvents has to do with the relative solubility of the delignifying chemicals in the cooking liquor. This was, however, at least in part disputed by Abbot & Bolker /83/. It would thereby seem that the effect is more refined than simply solubility. It is possible that the solvent effect is due to a change in behavior of the free water and thereby the cage effect of the water molecules surrounding the cooking chemicals.

Another possible explanation has to do with the heat transfer efficiency of the different solvents. Methanol vapor is significantly denser than steam at a given temperature, because the pressure is so much higher. This also means that methanol is a more efficient heat transporter, if one considers a case where hot steam condenses on cold chips at the saturation pressure of the vapor. This hypothesis is, however, disputed by the fact that the speeding up is also seen in liquid phase cooking and using a wide range of solvents with varying vapor pressures.

Based on the results and literature sources, possible hypotheses for the impact of methanol have been compiled into the following table:

**Table 19. Hypotheses concerning the effect of methanol on kraft pulping.**

<b>Theory</b>	<b>Supporting evidence</b>	<b>Contradictions</b>
Difference in solubility “Escaping tendency” / increased activity (~concentration)	Reaction speed for lignin increases as if concentration was higher	Hemicellulose yield higher with methanol The change of solvent does not drastically alter the effect although the solubility of NaOH is different in different solvents
Change in delignification reactions	Reaction speed increases, brightness increases, possible radicals in pulping- methanol known radical scavenger	Effect is not dependent on methanol being inside the wood
Change in the accessibility of lignin	Lignin is hydrophobic, methanol may work as a contact media despite low solubility of inorganic chemicals	Effect is not dependent on methanol being inside the wood
Change in diffusion of alkali / hydrosulphide	Organic solvents may “lower concentration” of wood constituents, increasing diffusion in wood cell wall	Water-methanol mixture has high viscosity, slows diffusion

Based on the results at hand, it is impossible to verify these hypotheses, so they have to be regarded as a possible starting point for future research.

### **5.11 Ideas for future research**

The present research leaves a lot of open questions. The most interesting one from the point of view of basic research must be the effect of organic solvents on pulping. There is a clear need for investigations into the basic properties of alkaline cooks in the presence of alcohols. At the moment, it is very hard even to find basic information on the behavior of different ionic species in aqueous solutions at the temperatures and concentrations used in kraft pulping. How an addition of organic solvents impact the behavior is far beyond current knowledge.

A further area that clearly needs more research is the dynamics of delignification inside the wood chip. Current research methods only give averages as wood is turned to fibers. Fiber Kappa Analysis and FT-IR measurements are a first step towards more reliable information. The same information ought to be obtainable for chips before defibration. One possibility would be to use UV spectroscopy of chips sliced in thickness direction. This should give an overall lignin concentration profile as well as lignin concentration of each fiber separately. The information could be used to make a refined diffusion/reaction model.

Almgren /59/ showed that extensive mass transfer takes place during vapor phase pulping (at least with slow heat-up). An experimental set-up with part of the chips being impregnated and another part not could be used to study the difference between methanol and water vapor phase pulping. A step in the same direction would be to just monitor the concentration of leached liquor.

As far as methanol vapor phase pulping is concerned, there is also a lot of scope for further research. A top priority is to study the quality and bleachability of the pulp produced with this pulping method. Should the fiber properties of the pulp be adequate, then larger scale testing should be performed to study the suitability of the process for industrial applications.

## **6 Conclusions**

In the present investigation the following methods of process investigation for softwood kraft pulping were identified:

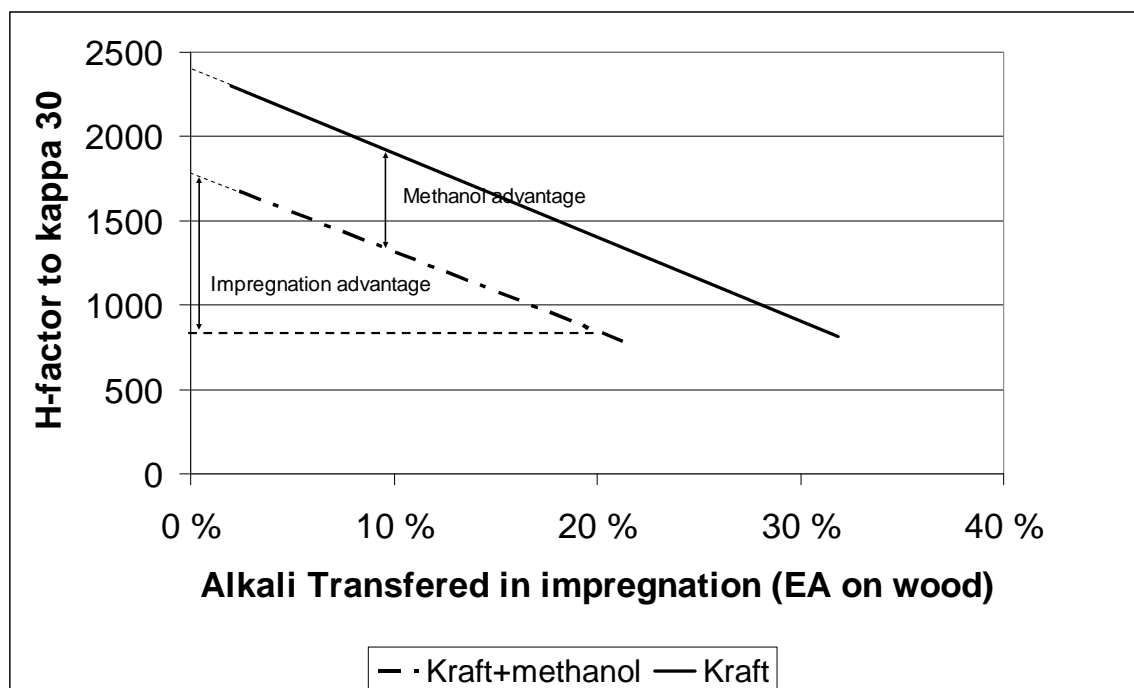
- Impregnation using high concentration
- the use of alcohols as heating media
- high temperature pulping

The methods can be combined and work in synergy. The most promising way identified taking advantage of the findings is a process with impregnation using high concentrations followed by methanol vapor phase pulping. The use of vapor phase minimizes the use of cooking chemicals in the cooking stage and the amount of methanol needed.

The benefits of using methanol vapor phase pulping include higher process yield and shorter process times. The use of high temperature further decreases the cooking time. A pre-requisite for the use of vapor phase and high temperature pulping is that sufficient impregnation is employed. Proper impregnation also decreases the pulping time, as seen in Figure 88. The obvious drawbacks of methanol vapor phase pulping are the need for an

extra chemical (methanol) and in the case of vapor phase pulping, the need to maintain a high effective alkali concentration in the impregnation liquor. Testing the feasibility of methanol re-generation was outside the scope of the present investigation.

Figure 88 is a schematic presentation of the results given in Figure 67, showing the relative benefits in pulping speed from improved impregnation and the use of methanol in softwood pulping to kappa number 30.



**Figure 88. Schematic presentation of the benefits of complete impregnation and methanol addition. The lines represent the relationship between the amount of alkali transferred to the wood in impregnation and the cooking time needed to reach kappa number 30 when cooking with constant positive end of cook alkalinity using standard kraft chemicals or kraft+methanol.**

In Figure 88 the dashed line shows the relationship between the amount of alkali transferred to the wood in impregnation and cooking time needed to kappa number 30 for kraft+methanol pulping, the solid line shows the relationship for water based kraft pulping. The distance between the two lines is the advantage in cooking speed from the use of methanol in the cooking stage. An interesting point is that the advantage is independent of whether the cooking is conducted in vapor-phase or liquid phase. The reason why vapor phase at first was seen as inherently faster than liquid phase pulping was that the use of vapor phase pulping makes it necessary to make impregnation “complete” before heating up as no mass-transfer can happen during the cooking stage.

In Table 20 the intensification potential of using complete impregnation and methanol addition has been calculated for three different cases. The first case without impregnation, the second represents penetration only and the third penetration and diffusion using a typical concentration of 40 g EA/l as NaOH.

**Table 20. Intensification potential by impregnation and use of methanol in pulping for cases without impregnation, with penetration only and with penetration and diffusion prior to heat-up. Calculations for transferred EA are based on the use of 40 g/l impregnation liquor and a total alkali need of 20% EA on wood.**

	No impregnation	Penetration only	Penetration + diffusion
EA transfered in impregnation	0 %	3.3 %	7.3 %
H-factor needed to reach 2.2% lignin yield	2400	2300	2000
Intensification potential by 100% impregnation using high concentration liquor (H needed: 1400)	42 %	39 %	15 %
Intensification potential by methanol addition	25 % (H needed: 1800)	26 % (H needed: 1700)	30 % (H needed: 1400)
Intensification potential by 100% impregnation and methanol vapor phase (H needed: 800)	67 %	65 %	60 %

Further improvements in pulping speed can be achieved by impregnating a surplus of alkali into the wood prior to heat-up, but as this leads to an increased strain on chemical recovery, it does not meet the criteria of an intensified process setup in the present research.

It is also possible to decrease the cooking time using high cooking temperature: increasing the cooking temperature from 165°C to 180°C would decrease the pulping time to reach an H-factor of 800 from 78 minutes by a further 70% to 23 minutes. The total decrease in cooking time when going from an unimpregnated cook at 165°C to a 100% pre-impregnated cook using methanol at 180°C using 5 minutes' heat-up would thus be from 4 hours to 23 minutes or >90%.

The use of high temperatures can be criticized on the grounds of increased heating demand. However, the use of vapor phase technology decreases the volume of liquor that has to be heated, so this aspect becomes less significant.

The current research does not answer the question of what brings about the positive effect of methanol on kraft pulping, nor was answering that question an objective of the present research. It does however seem clear that the explanation is something slightly more complex than the solubility and penetration theories presented in the past. Two interesting aspects that warrant further study are the effect of methanol on the amorphous wood polymers and the solvent effect on the hydration of inorganic chemicals in the cooking liquor.

Based on the results of the present investigation, it is clear that the kraft process, as currently employed, is highly inefficient. There is significant room for shortening reaction times, and the failure to do so cannot be justified with claims pertaining to process yield

or chemicals consumption. A mill taking advantage of the concepts presented would have some of the following benefits:

- Just in time manufacturing
- Agile reaction to changes in raw-material properties
- Increased possibilities to segregate raw-materials and produce tailored pulps

The present research also raises several questions about several basic assumptions widely used in kraft pulping research. For instance, the present research shows that higher chemical charges do not necessarily lead to extensive yield loss and that yield and pulp viscosity are not correlated over a wider range of processes. Also, based on the present research the widely used assumption that the concentration of cooking chemicals inside wood chips in pulping are in a straight relationship to the concentration of the surrounding liquor seems quite shaky. It is clearly time for pulping research to go back to fundamental science and make a more focused attempt at explaining the processes involved in wood delignification.



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- <sup>119</sup> Jääskeläinen, A-S., Nuopponen, M., Axelsson, P., Tenhunen, M., Löija, M. & Vuorinen, T., Determination of lignin distribution in pulps by FTIR ATR spectroscopy. *J. Pulp Pap. Sci.* 29(2003)10 p. 328-331.
- <sup>120</sup> Robinson, J.K., Gustafson, R.R., Callis, J.B. & Bruckner C., Measurement of kappa number variability on the fiber level. *Tappi J.* 1(2002)10 p. 3-8.
- <sup>121</sup> Milton J.S & Arnold J.C Introduction to probability and statistics. Internat. Ed. McGraw-Hill 1995 p. 349.
- <sup>122</sup> Finnish patent application no. 20055143

## **Heat Transfer and Temperature Profiles in Oil Bath Autoclave Digesters**

The calculations and results presented are compiled from a broader report written by Dr. Kari Kovasin in June 2000.

The purpose of these calculations is to calculate the probable internal temperature in a small oil heated autoclave used in pulping research.

### ***Starting values***

- Initial temperature inside the autoclave 20°C
- Target temperature inside the autoclave 165°C
- Autoclaves assumed to be cylinders of outside diameter 0.05 m and length 0.19 m. Wall thickness 0.003 m
- Autoclaves rotate in heating oil with a velocity of 14 rpm

### ***Heat transfer calculation principles***

#### **Heat transfer coefficients**

The most significant heat transfer resistance is outside of the autoclave, from the oil to the surface of the autoclave. The heat transfer resistance of the autoclave wall is practically insignificant and the inside heat resistance from the inner wall to the digester liquor gives a slight increase in total heat resistance. All factors have been taken into account in the calculations.

The heat transfer from the oil to the outer autoclave surface was calculated by means of forced convection. The flow regime is laminar and the suitable correlation for the outer side heat transfer coefficient is given in Perry's handbook, 5<sup>th</sup> Ed. Eq. 10-44 <sup>1</sup>/

The heat transfer inside the autoclave is governed by natural convection due to the limited flow in relation to the autoclave wall. A suitable correlation for the evaluation of the inner side heat transfer coefficient is given in Perry's handbook, eq. 10-32.

The total heat transfer coefficient was then calculated by means of eq. 10-115 of Perry.

#### **Case I: total mixing inside the bomb**

Considering the unsteady-state heat transfer during the heating up period, there are two limiting cases to be considered: either complete mixing inside the bomb or no mixing at all. The reality is somewhere in between these two extremes.

In case of complete mixing, the inside temperature in the digester liquor is the same in all place in the autoclave. The heat transfer can be calculated by preparing the unsteady state heat balance differential equation.

### **Case II: No liquor mixing inside the autoclave**

This alternative leads to heat conduction problem in cylindrical coordinates. The analytical solution would imply using Bessel functions and is as such solvable in a tedious but straightforward manner. However, there are useful graphical methods available for solving such problems. One good source is Janna's Engineering Heat Transfer –book <sup>2</sup>/.

In this no-mixing case, there is a temperature gradient inside the autoclave from the walls towards the centerline of the autoclave. The coldest point is the centerline and the hottest temperatures are at the autoclave walls. It is possible to estimate the average and the centerline temperatures by using Figs. 6.9a and 6.9b of <sup>2</sup>/.

### **Discussion**

The two methods give an idea of the behavior of the autoclave temperature in two extreme cases. Reality is probably somewhere in-between.

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<sup>1</sup> Perry, R.H., Chilton, C.H., Chemical Engineers' Handbook, 5<sup>th</sup> Ed., McGraw-Hill Publishing, New York, 1973

<sup>2</sup> Janna, W.S., Engineering Heat Transfer, PWS Engineering, Boston, 1986

### Time to temperature experiments

Cooking chemicals: White liquor + water (batch cook)

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	pH EoC, gEA/l	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, m/g	Brightness, % ISO
60	40	2	175	2302	96	25.0	9.2	21.1	1.4	43.9	0.0	1078	35.6
60	40	5	175	2310	97	25.0	10.0	19.9	1.3	43.7	0.0	1036	39.3
60	40	9	175	2318	92	25.0	9.5	23.5	1.6	45.4	0.0	1108	34.8
60	40	9	175	2335	95	25.0	9.6	21.9	1.5	44.5	0.0	1074	34.7
60	40	17	175	2320	92	25.0	9.4	23.7	1.6	45.1	0.3	1112	34.3
60	40	21	175	2305	88	25.0	10.2	23.1	1.6	44.4	0.0	1094	34.7
60	40	88	175	2295	79	25.0	10.5	22.7	1.5	44.6	0.1	1106	37.2
60	40	90	175	2301	84	25.0	13.1	23.3	1.6	44.6	0.0	1127	36.3

### Impregnation experiments

Cooking chemicals: White liquor + water (batch cook)

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	pH EoC, gEA/l	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, m/g	Brightness, % ISO
5	34	5	175	1799	73	21.1	6.4	44.0	3.2	48.2	1.2	--	29.9
5	31	5	175	1197	38	19.1	5.0	75.0	6.0	52.2	12.5	--	25.6
5	34	5	175	2218	94	21.1	6.3	31.3	2.2	46.2	0.1	1217	30.1
5	31	5	175	1520	61	19.3	6.0	59.1	4.6	50.5	4.9	--	28.2
5	31	88	175	1502	52	19.1	4.7	60.4	4.6	49.5	1.2	--	27.9
5	34	90	175	2209	81	21.1	5.7	30.2	2.1	45.8	0.0	1217	28.8
5	31	90	175	1805	65	19.1	4.8	44.4	3.2	47.0	0.1	--	31.1
60	34	4	175	2200	92	21.3	6.6	34.7	2.4	45.0	0.2	--	33.3
60	31	5	175	1501	62	19.1	5.4	61.4	4.7	50.4	6.5	--	26.4
60	31	6	175	1202	50	19.0	5.8	82.0	6.7	53.5	26.1	--	23.9
60	34	7	175	2001	84	21.3	6.5	37.8	2.7	46.5	0.6	1291	32.1
60	31	88	175	1401	46	19.1	5.0	62.9	4.7	49.3	2.1	--	27.9
60	31	90	175	1802	64	19.1	4.7	50.0	3.8	49.3	0.2	--	29.2
60	31	90	175	1497	50	19.1	5.6	56.8	4.3	49.4	1.0	--	28.1

## Solvent addition time to temperature

Cooking chemicals: White liquor + water + methanol (batch cook)

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	pH EoC, gEA/l	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, ml/g	Brightness, % ISO
60	40.8	4	175	2306	93	25.5	7.9	15.6	1.0	44.0	0.0	933	38.9
60	40.4	3	175	2315	95	25.3	7.2	15.5	1.0	43.7	0.0	878	39.4
60	40.4	10	175	2300	97	25.3	9.5	17.3	1.2	44.0	0.0	948	38.2
60	40.4	10	175	2308	95	25.3	7.3	15.0	1.0	43.8	0.0	863	40.4
60	40.4	20	175	2313	92	25.3	7.7	16.1	1.1	43.7	0.0	860	40.5
60	40.4	20	175	2309	96	25.3	7.3	15.1	1.0	43.5	0.0	825	41.1
60	40.4	88	175	2331	84	25.3	7.1	14.8	1.0	43.6	0.0	855	40.2
60	40.4	79	175	2316	80	25.3	3.6	13.9	0.9	43.0	0.0	825	40.9

## Impregnation experiments using solvent (Methanol impregnation)

Cooking chemicals: White liquor + water + methanol (batch cook)

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	pH EoC, gEA/l	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, ml/g	Brightness, % ISO
60	40.4	5	175	1809	75	25.3	7.6	21.5	1.5	45.1	0.1	979	38.0
60	40.4	5	175	1773	73	25.3	8.8	21.7	1.5	45.7	0.2	955	36.7
60	40.4	10	175	1759	76	25.3	7.9	21.9	1.5	45.2	0.2	936	37.2
60	40.8	22	175	1820	72	25.5	8.4	18.4	1.3	44.6	0.0	908	39.8
60	40.8	90	175	1763	59	25.5	9.7	17.7	1.2	44.7	0.0	913	39.9
60	34.8	5	175	1618	66	21.8	6.7	27.3	1.9	46.5	0.2	1092	35.7
60	32.0	7	175	1308	52	20.0	4.8	38.4	2.9	49.1	1.6	1245	32.1
60	31.8	6	175	918	36	19.9	6.3	54.6	4.3	51.8	6.8	1275	29.9
60	31.8	5	175	607	23	19.9	7.7	75.4	6.4	55.3	17.7	--	26.4
60	30.0	4	175	548	21	18.8	6.5	83.4	7.5	58.9	34.9	--	25.4
5	37	4	175	1854	77	23.1	5.6	24.8	1.8	46.8	0.2	1072	36.1
5	34.4	4	175	1754	72	21.5	4.8	29.4	2.2	48.0	0.8	1147	34.1
5	34.8	5	175	1578	65	21.8	7.0	30.3	2.2	48.1	0.7	1125	29.3
5	34.4	6	175	1606	66	21.5	4.4	32.1	2.4	48.5	0.5	1184	33.9
5	32.0	4	175	906	37	20.0	5.2	53.6	4.4	54.0	8.1	--	29.3
5	32.2	4	175	800	32	20.1	6.1	60.3	5.0	54.6	10.6	--	28.8



## Methanol displacement (Methanol cooking)

Cooking chemicals: (White liquor + water) / methanol displacement

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	pH 11 EoC, gEA/l	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, ml/g	Brightness, % ISO
60	66.8	3	175	1995	71	25.1	12.3	12.7	0.8	42.1	0.0	621	43.3
60	66.8	7	175	2029	83	25.1	10.3	13.6	0.9	43.5	0.0	721	43.6
60	66.8	21	175	1701	68	25.1	13.7	13.4	0.9	42.9	0.0	763	44.5
60	56.8	4	175	1695	71	23.4	--	18.8	1.3	44.7	0.0	901	40.4
60	56.8	3	175	1607	58	21.3	6.0	21.9	1.5	45.4	0.0	842	38.3
60	56.8	4	175	1595	66	21.3	7.5	20.8	1.5	45.6	0.0	952	40.2
60	56.8	21	175	1625	64	21.3	7.7	20.1	1.4	44.9	0.0	987	40.0
60	56.8	10	175	1595	66	21.3	7.3	21.4	1.5	45.1	0.0	985	38.9
60	56.8	10	175	1598	64	21.3	7.2	21.7	1.5	46.1	0.0	993	38.6
60	56.4	87	175	1625	56	21.2	7.9	18.7	1.3	44.8	0.0	975	40.6
60	56.4	19	175	1620	63	21.2	8.8	18.7	1.3	45.2	0.0	956	40.6
60	56.4	90	175	1607	63	21.2	8.4	18.8	1.3	44.8	0.0	991	41.0
60	51.6	90	175	1207	38	19.4	6.4	29.4	2.1	46.5	0.0	1154	38.0
60	45.4	90	175	702	18	17.0	4.5	66.8	5.3	51.7	4.0	--	29.4
60	48	90	175	695	17	18.0	6.5	57.1	4.4	50.7	0.8	--	30.6
60	50.4	6	175	1201	48	18.9	5.8	31.5	2.3	47.5	0.1	1153	34.8
60	51.6	5	175	1193	56	19.4	5.5	42.2	3.1	48.2	0.3	--	31.3
60	51.6	6	175	1199	49	19.4	6.0	30.7	2.2	47.0	0.1	1113	35.9
60	48.0	5	175	909	36	18.0	6.1	44.5	3.3	48.9	0.5	1240	32.5
60	45.6	5	175	708	28	17.1	6.8	60.8	4.8	51.8	3.1	--	30.4
60	44.0	5	175	520	19	16.5	6.3	86.2	7.4	56.1	29.9	--	26.8
60	48.0	90	175	897	26	18.0	5.7	46.2	3.5	48.9	0.0	--	32.9
1day	54.2	5	175	1306	53	20.3	5.2	40.7	3.0	48.9	0.0	--	31.3
1day	45.6	5	175	806	33	17.1	2.8	68.0	5.5	53.1	14.3	--	25.7

1day	54.2	5	175	1111	44	20.3	2.9	41.5	3.2	49.9	0.2	--	31.8
1day	54.2	5	175	1007	41	20.3	3.6	43.3	3.3	50.5	0.1	--	30.1
1day	54.2	5	175	802	32	20.3	2.8	53.5	4.5	54.4	0.9	--	28.2
1day	50.0	5	175	1006	41	18.8	1.8	52.0	4.1	52.1	0.7	--	28.1
1day	50.0	5	175	796	33	18.8	2.8	62.1	5.1	53.6	3.0	--	26.8
3day	54.2	5	175	1369	56	20.3	2.2	33.0	2.5	49.0	0.0	--	32.4
3day	45.6	5	175	805	29	17.1	1.2	74.1	6.2	54.9	29.3	--	24.7
4day	54.2	5	175	1304	53	20.3	2.3	35.9	2.8	50.1	0.0	--	32.2
4day	54.2	5	175	1001	41	20.3	3.7	43.3	3.4	51.2	0.0	--	30.6
4day	54.2	5	175	802	33	20.3	5.4	56.0	4.5	52.7	0.5	--	29.4
4day	45.6	5	175	804	33	17.1	1.4	69.4	5.8	54.3	7.9	--	24.1
7day	54.2	5	175	1300	54	20.3	3.6	34.2	2.5	48.7	0.0	--	31.0
7day	50.0	5	175	802	33	18.8	2.8	62.0	5.0	52.9	2.6	--	26.7
5	54.2	5	175	1515	61	20.3	4.8	31.3	2.3	47.8	0.3	1108	34.9
5	54.2	5	175	1320	56	20.3	6.6	32.8	2.4	47.1	0.3	1121	35.5
5	51.6	5	175	1206	51	19.4	5.0	38.8	3.0	50.0	0.4	1173	33.9
5	51.6	6	175	1000	40	19.4	6.0	42.6	3.2	49.8	1.3	--	32.6
5	45.6	5	175	803	31	17.1	3.5	66.2	5.6	55.1	10.9	--	27.8
5	45.6	5	175	701	27	17.1	4.2	71.7	6.2	56.3	10.4	--	27.9
5	54.2	90	175	1300	36	20.3	4.6	34.0	2.5	47.3	0.1	--	36.1
5	45.6	90	175	998	30	17.1	3.7	49.4	3.8	50.1	0.3	--	31.2
5	45.6	90	175	802	21	17.1	4.2	58.3	4.5	51.0	1.5	--	29.7
5	45.6	90	175	701	18	17.1	3.2	73.8	6.0	53.4	14.6	--	27.4
5	45.6	90	175	553	10	17.1	3.7	90.2	7.6	55.3	32.3	--	25.3

## Vapor phase cooking (MeOH-vapor, water steam, kraft liquid reference)

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	Alkali to cook, % EA as NaOH	EOC, gEAl pH 11	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, mI/g	Brightness, % ISO
MeOH vapor														
15	120.4	9	175	806	30	45.2 %	14.9 %	4.1	40.3	3.4	54.6	2.31		30.30
68	89.6	5	175	1002	37	38.1 %	16.0 %	4.8	33.5	2.6	51.4	0.55	1089	32.11
68	94.8	5	175	1009	38	40.3 %	18.7 %	3.5	32.8	2.6	51.7	0.46	1136	32.99
60	95.0	7	175	998	39	40.4 %	16.7 %	4.7	36.1	2.9	52.66	1.87	1111	31.01
60	95.0	5	175	711	23	40.4 %	16.7 %	4.9	38.5	3.1	52.57	1.14	1120	32.11
60	100.0	5	175	1002	39	42.5 %	18.4 %	6.0	30.2	2.4	51.07	0.97	1047	33.43
60	100.0	5	175	700	26	42.5 %	18.8 %	6.0	39.4	3.2	52.65	1.21	1138	31.58
60	100.0	6	175	505	18	42.5 %	19.0 %	10.0	43.9	3.6	53.5	1.8	-	31.23
60	100.0	6	175	310	11	42.5 %	17.7 %	9.5	71.9	6.5	58.75	8.06	-	26.70
60	100.0	6	175	500	18	42.5 %	16.9 %	8.1	48.8	3.9	52.66	2.22	-	30.79
60	100.0	5	175	1302	52	42.5 %	18.0 %	6.4	27.0	2.1	51.15	0.49	1006	33.87
60	100.0	4	175	1650	67	42.5 %	17.8 %	5.5	22.3	1.7	49.61	0.41	923	34.66
60	95.0	9	175	405	13	40.4 %	17.5 %	8.7	55.6	4.8	56.01	1.53	-	29.16
60	100.0	7	175	702	26	42.5 %	17.9 %	7.5	36.9	3.0	52.97	0.74	-	33.00
60	96.8	8	175	550	20	41.1 %	17.7 %	7.0	45.5	3.7	52.97	1.28	-	30.48
60	93.2	7	175	254	7	39.6 %	16.8 %	7.2	87.7	8.2	61.05	21.39	-	24.31
1080	100.0	4	175	995	39	42.5 %	19.9 %	9.6	21.8	1.6	48.31	0.28	862	38.36
Water steam														
68	95.2	7	175	1663	65	40.5 %	18.2 %	5.8	31.6	2.4	50.2	0.28		31.22
68	94.4	5	175	1664	68	40.1 %	17.5 %	4.3	28.9	2.2	49.4	0.21	1190	32.53
65	95.2	6	175	1651	69	40.5 %	17.8 %	5.3	44.2	3.5	51.9	0.62	-	29.34
68	100.0	6	175	1659	70	42.5 %	18.3 %	7.0	27.5	2.1	49.02	0.03	1077	34.36
68	100.0	6	175	1197	49	42.5 %	17.7 %	7.2	39.6	3.1	51.91	0.3	1211	30.53
60	100.0	5	175	803	34	42.5 %	18.2 %	9.6	49.1	4.0	52.96	0.44	-	30.25
60	100.0	5	175	1654	69	42.5 %	18.4 %	5.2	32.6	2.5	50.54	0.24	1089	31.64
60	100.0	5	175	1206	40	42.5 %	17.2 %	7.2	42.8	3.2	49.42	1.59	-	30.99
60	100.0	5	175	601	27	42.5 %	17.2 %	9.6	72.3	5.9	53.27	10.48	-	28.86
60	100.0	5	175	1001	40	42.5 %	18.6 %	7.5	48.2	3.9	53.51	0.75	-	29.03
60	95.0	7	175	598	24	40.4 %	16.8 %	9.2	71.6	6.2	56.24	4.22	-	26.31
60	106.8	8	175	1799	74	45.4 %	19.0 %	6.4	22.5	1.7	48.65	0.06	1063	35.35

## Kraft reference (batch cook)

60	44.0	5	175	2312	97	22.0 %	6.2	25.2	1.8	47.8	0.01	1167	34.60
60	45.0	5	175	2300	96	22.5 %	7.4	22.8	1.7	47.4	0.06	1115	35.50
60	43.0	6	175	2171	90	21.5 %	5.9	27.9	2.1	48.1	0.04	1227	34.10
60	41.0	5	175	1998	83	20.3 %	5.7	33.2	2.5	49.5	0.11	1283	31.66
60	39.0	5	175	1800	75	19.5 %	5.0	42.4	3.3	50.7	0.61		28.55
60	38.0	5	175	1598	67	19.0 %	5.0	51.7	4.1	52.3	1.79		27.68
60	44.0	62	175	2163	81	22.0 %	8.7	20.2	1.4	46.3	0.005	1104	37.41
60	38.0	60	175	1604	61	19.0 %	5.6	41.8	3.2	50.2	0.05		30.36
60	43.0	7	175	2147	88	21.5 %	7.8	25.7	1.9	48.2	0.02	1181	33.35
60	43.0	6	175	2002	86	21.5 %	6.8	28.2	2.1	49.28	0.08	1209	33.05
60	43.0	7	175	1499	63	21.5 %	8.8	42.3	3.3	51.67	1.19	-	30.20
60	43.0	7	175	998	41	21.5 %	10.1	62.3	5.2	54.67	4.11	-	27.08
60	43.0	6	175	499	20	21.5 %	13.1	99.3	9.5	62.82	41.67	-	21.80

## Study on impregnation, constant cooking time

Kraft impregnation, methanol vapor cooking

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp., C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	Alkali to cook, % EA as NaOH	pH 11	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, ml/g	Brightness, % ISO	Impregnation temp., C
<b>Statistical study. Param: imp. T, imp. EA, imp. time, H-factor.</b>															
<i>Impregnation temp 25C</i>															
15	40.0	8	175	996	37	17.0 %	6.1 %	-	137.2	16.1	76.9	70.5	-	14.0	25
68	80.0	8	175	996*	37	34.0 %	15.5 %	4.5	42.7	3.5	53.0	1.7	-	29.3	25
15	120.0	8	175	1006	37	51.0 %	16.5 %	5.9	30.3	2.4	51.9	0.7	-	33.3	25
120	40.0	8	175	1011	38	17.0 %	7.9 %	0.0	128.3	14.0	71.2	62.5	-	-	25
68	80.0	9	175	1019	39	34.0 %	14.8 %	1.8	46.1	3.8	53.7	1.7	-	28.5	25
120	120.0	7	175	1010	38	51.0 %	21.0 %	14.0	20.2	1.6	50.7	0.1	819	36.7	25
68	40.0	7	175	1007	37	17.0 %	8.0 %	0.0	127.0	14.2	73.1	65.4	-	13.3	25
68	80.0	7	175	1003	37	34.0 %	13.8 %	1.2	45.6	3.7	53.5	1.5	-	29.0	25
68	120.0	12	175	1003	38	51.0 %	19.8 %	11.5	21.4	1.7	50.5	0.2	859	36.5	25
15	80.0	9	175	1006	38	34.0 %	11.3 %	0.0	72.4	6.6	60.0	16.6	-	23.3	25
120	80.0	7	175	1002	39	34.0 %	14.6 %	1.4	48.2	4.0	54.5	2.4	-	27.8	25

*Impregantion temp 80C*

15	40.0	5	175	1003	36	17.0 %	7.6 %	-	138.2	15.6	73.9	66.6	-	14.9	80
68	80.0	4	175	1001	36	34.0 %	15.3 %	2.3	45.1	3.7	53.7	3.8	-	28.9	80
15	120.0	6	175	997	39	51.0 %	18.8 %	9.1	26.6	2.1	51.7	0.3	958	33.7	80
68	80.0	5	175	1008	36	34.0 %	14.0 %	3.1	40.8	3.3	52.7	1.1	-	29.8	80
120	40.0	6	175	998	37	17.0 %	8.6 %	0.0	123.3	13.1	69.4	58.4	-	14.6	80
120	120.0	5	175	998	38	51.0 %	21.5 %	14.1	21.8	1.6	49.4	0.2	-	36.6	80
94	56.9	6	175	999	37	24.2 %	10.1 %	0.0	76.8	6.9	59.0	24.3	-	22.0	80
68	40.0	5	175	1061	37	17.0 %	8.0 %	0.0	121.7	13.3	71.6	66.0	-	-	80
68	80.0	5	175	1003	38	34.0 %	15.0 %	1.4	44.4	3.6	53.6	2.4	-	27.4	80
68	120.0	8	175	1003	38	51.0 %	19.4 %	12.6	22.6	1.7	49.8	0.1	848	36.7	80
15	80.0	5	175	1014	39	34.0 %	13.5 %	0.5	55.0	4.7	55.7	7.2	-	26.9	80
120	80.0	5	175	1002	39	34.0 %	15.5 %	3.1	40.2	3.2	52.4	1.1	-	30.5	80
41	99.6	6	175	1008	39	42.3 %	17.4 %	6.8	30.0	2.3	51.1	0.3	1050	33.0	80
41	110.4	5	175	1001	39	46.9 %	18.1 %	8.8	26.0	2.0	51.0	0.4	948	35.2	80
41	89.6	6	175	1003	39	38.1 %	15.9 %	4.6	34.3	2.7	51.7	0.7	1118	31.9	80
68	89.6	5	175	1002	37	38.1 %	16.0 %	4.8	33.5	2.6	51.4	0.6	1089	32.1	80
68	85.2	5	175	999	36	36.2 %	15.0 %	2.8	40.4	3.2	52.5	1.8	1194	29.6	80
68	74.8	6	175	1004	38	31.8 %	13.3 %	0.5	49.8	4.1	54.4	4.5	-	27.6	80
68	69.6	5	175	1000	38	29.6 %	12.7 %	0.0	56.8	4.8	55.6	9.0	-	25.6	80
68	64.8	5	175	1022	38	27.5 %	12.8 %	0.0	64.0	5.6	57.3	7.9	-	23.9	80
68	59.6	5	175	1001	39	25.3 %	11.1 %	0.0	78.6	7.3	60.8	24.9	-	20.7	80
68	55.6	5	175	1002	39	23.6 %	10.9 %	0.0	80.4	7.3	59.6	28.2	-	21.4	80
68	80.0	7	175	1003	40	34.0 %	14.8 %	1.8	41.2	3.3	52.5	1.0	-	29.4	80
68	80.0	6	175	996	39	34.0 %	14.9 %	0.6	39.3	3.2	53.0	1.5	1161	30.3	80

*Impregnation temp 80C, varyig H-factor*

68	80.0	5	175	610	23	34.0 %	14.6 %	3.3	68.4	5.9	56.4	5.2	-	26.1	80
68	80.0	5	175	801	30	34.0 %	15.0 %	3.1	49.0	4.1	54.8	3.7	-	28.1	80
68	80.0	7	175	1003	40	34.0 %	14.8 %	1.8	41.2	3.3	52.5	1.0	-	29.4	80
68	80.0	5	175	1200	48	34.0 %	14.0 %	1.6	39.9	3.2	52.7	1.3	-	28.7	80
68	80.0	5	175	1405	54	34.0 %	14.4 %	1.3	33.2	2.6	51.7	1.1	-	30.4	80

## Study on cooking temepreature

Kraft impregnation, methanol vapor cooking

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	Alkali to cook, % EA as NaOH	CoC, gEA/l pH 11	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, ml/g	Brightness, % ISO
165C														
60	95.0	5	165	309	26	40.4 %	16.9 %	7.8	73.0	6.6	59.22	4.87	-	27.06
60	95.0	5	165	505	45	40.4 %	16.2 %	9.2	46.4	3.9	55.19	0.86	-	31.28
60	100.0	5	165	703	64	42.5 %	17.9 %	7.9	36.6	3.0	52.88	0.99	1189	33.19
60	104.4	5	165	1003	92	44.4 %	18.6 %	9.2	25.0	2.0	51.23	0.14	1089	36.29
60	102.8	7	165	1005	92	43.7 %	17.7 %	8.6	24.2	1.9	51.01	0.16	1056	35.52
60	105.2	5	165	1296	119	44.7 %	17.5 %	7.0	21.8	1.7	50.3	0.22	966	36.65
60	95.0	5	165	449	38	40.4 %	17.4 %	8.3	56.7	4.8	55.56	2.31	-	29.53
60	95.0	6	165	251	21	40.4 %	17.4 %	8.4	80.6	7.3	59.49	10.19	-	25.26
60	94.8	7	165	298	26	40.3 %	17.2 %	10.4	67.5	6.0	58.59	3.81	-	28.27
60	100.0	5	165	697	65	42.5 %	20.4 %	10.6	34.2	2.6	50.4	0.35	1148	34.85
60	104.4	10	165	1001	94	44.4 %	17.3 %	7.6	27.3	2.1	49.97	0.84	1035	31.59
60	104.3	10	165	1022	99	44.3 %	15.3 %	6.9	24.1	1.8	49.38	0.44	1013	32.34
185C														
60	105.2	10	185	1050	15	44.7 %	19.0 %	7.6	24.5	1.9	50.22	0.55	883	36.32
60	100.0	10	185	709	9	42.5 %	17.6 %	8.1	34.5	2.7	52.08	1.26	1009	33.92
60	95.0	11	185	505	6	40.4 %	19.3 %	7.2	49.3	4.1	54.2	1.29	-	30.44
60	95.0	11	185	304	2	40.4 %	17.5 %	8.1	69.0	6.1	57.57	6.11	-	26.70
60	95.0	14	185	296	1	40.4 %	17.2 %	9.3	69.2	6.1	57.48	3.98	-	27.38
155C														
60	89.6	4	155	101	18	38.1 %	17.0 %	9.4	114.3	11.5	65.91	58.1	-	22.55
60	89.6	5	155	250	53	38.1 %	17.3 %	7.5	88.6	8.0	58.83	30.81	-	25.37
60	89.6	5	155	599	133	38.1 %	16.4 %	4.8	46.0	3.7	53.16	1.43	-	31.40

## Thick chips

Impregnation time, min	Imp. liquor EA (pH 9.5), g/l	Heat-up, min	Cooking temp, C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	Alkali to cook, % EA as NaOH	pH 11 EoC, gEA/l	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, ml/g	Brightness, % ISO
Heartwood														
Kraft liquid phase														
60	33.0	7	175	2760	118	23.6 %		8.4	37.1	2.7	47.1	7.72	1044	31.91
60	37.5	10	175	3150	130	26.8 %		11.5	26.2	1.7	41.845	3.29	927	34.86
60	36.0	11	175	3000	125	25.7 %		11.6	29.0	1.9	43.36	5.72	959	34.46
Methanol vapor														
60	125.2	8	175	1316	51	78.2 %	19.3 %	8.9	30.0	2.2	48.875	9.67	751	34.54
60	119.6	11	175	1100	43	74.7 %	15.9 %	5.9	40.5	3.4	54.67	18.34	877	30.79
60	128.0	10	175	1512	58	80.2 %	17.0 %	6.4	40.1	3.6	57.98	20.97	830	29.93
Water steam														
60	130.0	9	175	2200	93	81.2 %	16.8 %	6.6	49.1	3.8	50.98	22.94	900	28.48
60	129.6	10	175	2398	98	81.0 %	18.5 %	6.5	48.1	3.8	51.985	22.99	890	28.91
60	134.4	12	175	2404	99	84.2 %	18.0 %	7.6	40.3	3.1	50.1	17.54	860	30.39
60	140.0	14	175	2610	107	87.5 %	11.9 %	7.4	42.8	3.4	51.42	19.26	-	28.93
60	142.4	10	175	3003	126	89.2 %	19.3 %	7.3	33.4	2.6	50.53	15.20	806	31.45
Sapwood														
Kraft liquid phase														
60	43.6	9	175	2206	89	26.0 %		17.9	28.5	2.0	46.73	4.66	1033	33.99
60	36.4	10	175	3015	124	26.0 %		?	21.2	1.4	44.535	2.365	912	35.46
60	32.0	9	175	2509	104	22.9 %		8.0	39.5	3.0	50.0	9.445	1105	29.78
60	33.0	9	175	2756	114	23.6 %		8.5	36.9	2.8	48.8	8.91	1089	29.97
Methanol vapor														
60	100.0	8	175	1648	66	62.6 %	12.7 %	3.0	48.8	4.2	56.5	22.57	-	24.23
60	120.0	8	175	1999	87	75.2 %	17.0 %	7.3	35.5	2.7	49.81	8.28	925	30.63
60	130.0	8	175	2208	92	81.5 %	20.9 %	10.4	30.5	2.2	48.23	7.28	890	32.48
Water steam														
60	100.0	6	175	1064	41	62.6 %	17.3 %	3.0	39.6	3.3	54.48	9.87	1029	30.01
60	108.0	7	175	1099	42	67.6 %	16.3 %	5.4	36.6	2.9	51.51	7.35	958	30.37
60	115.0	8	175	1359	72	71.8 %	15.9 %	3.6	27.2	2.0	49.27	5.12	814	31.67
60	125.2	5	175	1097	45	78.3 %	19.4 %	5.2	28.4	2.2	50.96	5.1	878	33.40
60	129.6	10	175	1005	37	81.1 %	14.0 %	7.2	28.2	2.2	50.15	7.19	809	34.66

## Solvents other than methanol

Kraft impregnation, solvent vapor cooking

Impregnation time, min	Imp. liquor EA (pH 6.5), g/l	Heat-up, min	Cooking temp, °C	H-Factors acquired	Cooking time, min	Alkali Charge, % EA as NaOH	Alkali to cook, % EA as NaOH	pH 11	Kappa number	Lignin yield, % on wood	Total Yield, % on wood	Rejects, % on wood	Viscosity, mPa/g	Brightness, % ISO	Solvent used
60	100.0	5	175	1000	38	42.5 %	18.6 %	4.0	28.2	2.2	51.35	0.86	914	35.38	1-propanol
60	100.0	9	175	1658	67	42.5 %	17.7 %	3.8	19.6	1.5	49.03	0.42	807	39.76	1-propanol
60	108.0	8	175	1000	39	45.9 %	18.5 %	7.9	22.7	1.7	50.05	0.22	841	38.96	1-propanol
60	100.0	6	175	700	29	42.5 %	17.5 %	6.9	35.0	2.8	53.16	1.05	1030	35.15	1-propanol
60	95.0	7	175	491	19	40.4 %	16.8 %	7.9	48.3	4.0	53.94	1.17	-	32.33	1-propanol
60	89.6	7	175	302	10	38.1 %	16.3 %	10.1	77.1	6.9	58.62	11.75	-	27.20	1-propanol
60	87.2	8	175	312	12	37.1 %	16.0 %	4.4	81.7	7.5	59.84	15.03	-	27.04	1-propanol
60	95.0	7	175	377	13	40.4 %	16.5 %	7.5	57.8	5.0	56.22	2.05	-	31.06	1-propanol
60	100.0	8	175	1002	38	42.5 %	17.3 %	6.0	27.2	2.1	51.05	0.38	929	35.10	2-propanol
60	100.0	6	175	1650	67	42.5 %	18.0 %	4.1	22.5	1.7	50.33	0.18	897	35.09	2-propanol
60	94.4	9	175	508	7	40.1 %	16.9 %	7.0	56.6	4.9	56.29	2.76	-	29.91	2-propanol
60	100.0	5	175	1655	66	42.5 %	16.1 %	8.7	41.4	2.7	43.34	0.17	-	19.86	Acetone
60	100.0	5	175	1000	40	42.5 %	18.1 %	8.7	43.0	3.3	50.31	0.11	-	20.07	Acetone
60	100.0	7	175	2003	82	42.5 %	17.7 %	7.0	40.7	2.9	46.97	0.14	-	18.46	Acetone
60	92.0	11	175	1006	35	39.1 %	16.1 %	7.8	48.4	3.8	51.18	0.12	-	19.68	Acetone
60	86.8	8	175	726	24	36.9 %	15.6 %	7.3	68.6	5.8	55.6	0.97	-	19.15	Acetone
60	84.0	7	175	518	17	35.7 %	14.9 %	8.1	71.0	6.3	57.82	3.54	-	19.42	Acetone
60	80.0	8	175	303	9	34.0 %	13.7 %	9.8	95.6	9.1	62.17	24.05	-	18.13	Acetone
60	74.8	8	175	336	9	31.8 %	13.4 %	6.3	96.9	9.4	63.73	17	-	16.45	Acetone
60	100.0	5	175	1630	67	42.5 %	16.9 %	5.3	20.3	1.5	47.24	0.28	746	37.73	Ethanol
60	100.0	5	175	1005	40	42.5 %	19.1 %	6.0	28.6	2.3	52.04	0.51	942	36.09	Ethanol
60	100.0	7	175	299	10	42.5 %	18.5 %	8.4	64.4	5.8	58.89	3.46	-	29.29	Ethanol
60	70.0	8	175	1007	38	29.7 %	13.2 %	0.0	53.0	4.5	56.04	6.1	897	27.96	Ethanol
60	85.0	6	175	1005	37	36.1 %	15.6 %	2.4	39.3	3.2	52.96	2.05	1151	31.64	Ethanol
60	100.0	8	175	603	22	42.5 %	18.3 %	8.3	39.7	3.3	54.29	1.98	1016	33.29	Ethanol
60	95.2	13	175	609	18	40.5 %	16.8 %	5.8	42.7	3.5	54.31	2.29	-	33.28	Ethanol
60	92.8	7	175	507	17	39.4 %	15.8 %	4.0	54.4	4.7	57.06	3.51	-	30.52	Ethanol
60	95.2	8	175	500	16	40.5 %	17.1 %	5.0	55.1	4.7	56.31	3.34	-	30.06	Ethanol
60	92.8	8	175	300	10	39.4 %	16.7 %	7.3	70.4	6.2	58.02	4.41	-	28.02	Ethanol
60	89.0	8	175	202	5	37.8 %	15.9 %	6.7	96.1	9.3	63.47	31.64	-	25.20	Ethanol
60	92.8	7	175	236	7	39.4 %	17.7 %	16.7	83.7	7.7	60.41	20.61	-	26.87	Ethanol
60	100.0	6	175	1654	71	42.5 %	17.0 %	2.9	25.3	1.8	45.45	0.49	804	34.04	N-butanol
60	100.0	5	175	1008	44	42.5 %	19.7 %	6.0	36.5	2.9	51.99	1.13	1041	31.93	N-butanol
60	100.0	5	175	1630	67	42.5 %	17.6 %	6.1	24.0	1.8	49.63	0.19	883	33.77	T-butanol
60	100.0	5	175	1000	41	42.5 %	18.3 %	4.6	31.9	2.5	51.05	0.49	964	33.30	T-butanol