Effects of pre-steaming in acid sulphite pulping

Effektar av basing i sure sulfittkok

Major subject thesis

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<u>SUM</u>	<u>IMARY</u> 5
<u>SAM</u>	IANDRAG
<u>INT</u>	RODUCTION7
1.1 1.1.1	BACKGROUND7 Front end of sulphite pulping7
1.1.2	Impregnation
1.1.3	Penetration research
1.1.4	Factors affecting penetration9
1.1.5	Pre-steaming11
1.1.6	Factors affecting efficiency of pre-steaming11
1.2 1.3 1.4	FINDINGS AT BORREGAARD11THE PROBLEM13OBJECTIVES13
<u>ME</u>	THOD & MATERIAL
2.1 2.2 2.3 2.3.1	STRUCTURE 14 DATA ANALYSIS 14 EXPERIMENT A: SCREENING FOR EFFECTS OF TEMPERATURE AND DURATION 15 15 Experimental design 15
2.3.2	Raw material
2.3.3	Equipment17
2.3.4	Experimental procedure19
2.4 2.4.1	EXPERIMENT B: DERIVATE COOKING IN AUTOCLAVES
2.4.2	Raw material
2.4.3	Equipment 22
2.4.4	Experimental procedure
2.5.1	Experimental design25

2.5.2	2 Raw material	
2.5.3	3 Equipment	
2.5.4	4 Experimental procedure	
<u>RES</u>	SULTS & DISCUSSION	29
3.1	PRESTEAMING EXPERIMENTS	
3.1.1	Net change - effects of duration	
3.1.2	2 Kappa - effects of duration	
3.1.3	3 Net change - effects of temperature	
3.1.4	4 Kappa - effects of temperature	
3.2 3.2.1	EXPERIMENT C: COOKING SIMULATIONS Properties of the pulp	
3.3	A FACTORIAL VIEW – ERRORS IN EXPERIMENTS	
3.3.1	1 Factors related to the wood	
<u>CON</u>	NCLUSION	
<u>REF</u>	FERENCES	
ANN	NEX A	

Summary

In theory pre-steaming should facilitate penetration of cooking liquor, achieving less reject, uniform pulp, reduce batch cycles and increase batch capacity. This paper debate effects of pre-steaming with emphasis on the impregnation and Kappa number. Effect of steaming time, steaming temperature, and impregnation time and liquor temperature was investigated at several levels.

The background for this paper was Borregaard Industries Ltd (Sarpsborg) observing a high level of reject during derivate cooking, producing special qualities of cellulose. The explanation was improper impregnation. In experiments emphasising on pre-steaming Borregaard found higher Kappa numbers and a lowering of the viscosity. The conclusion was that pre-steaming is more harmful than beneficiary, and probably caused by dilution of the cooking liquor.

The controversy between theory and observations was investigated in three different laboratory experiments. In a new laboratory digester, raw sawmill chips were presteamed with saturated steam and impregnated with water. The chips were screened for possible effects of pre-steaming by cooking the air-dried chips in autoclaves. Finally, simulations of a full scale cooking process were carried out in the laboratory digester, comparing pre-steaming for dissolving and derivate cooking.

Pre-steaming trials verified significant effects of liquor temperature and steaming temperature. The effect is caused by difference in temperature, probably most effective if the chips hold a temperature above 100°C and cold liquor is added. On this basis it can be concluded that pre-steaming is an effective technique to achieve a higher degree of liquor penetration. However, autoclave cooking spotted a possible constraint of steaming at high temperature. Trends indicate that high temperatures during steaming could cause higher Kappa number.

It was concluded that pre-steaming is possible in small digesters, but could be difficult in the 120-ton batch boiler at Borregaard. In this case, the pre-steaming process would have to be an independent step in the production line.

Samandrag

I teorien skal basing leggje tilhøva til rette for auka inntrenging av kokesyre og der igjennom gje lågare silutskot, jamnare kokt masse, redusere koketida og gje større kokarkapasitet. Denne oppgåva drøftar effekten av basing med omsyn til responsane impregnering, Kappa-tal og kokesyresamansetning. Basingstid, basings temperatur, impregneringstid og væsketemperatur vart undersøkt på fleire nivå.

Bakgrunnen for oppgåva var Borregaard Industries Ltd. i Sarpsborg sine observasjonar av høgt silutskot etter derivatkoking av nokre kvalitetar spesialcellulose. Forklaringa var manglande impregnering. Med omsyn på basingssteget, gjennomførde Borregaard fabrikkforsøk der resultatet var høgre Kappa-tal og lægre viskositet. På dette grunnlaget konkluderte fabrikken med at basing truleg gjorde meir skade enn gagn, og at uttynning av kokesyra var årsaka.

Uovereinstemminga mellom teori og observasjonar vart undersøkt i tre laboratorieforsøk. Rå sagbruksflis vart basa med metta vassdamp og impregnert med vatn i ein ny type laboratoriekokar. Ved å tørke flisa og koke ho i autoklavar, vart flisa undersøkt for eventuelle påverknader av basinga. Til slutt vart basing for dissolving og derivatkok samanlikna ved å simulere kokeprosessen i ein spesiallaga kokar. Det vart påvist signifikant høgre væskeopptak i flisa for basing ved 105°C enn ved 80°C. Basing med påfølgjande impregnering ved vasstemperatur på 50°C gav signifikant høgre væskeopptak enn ved væsketemperatur på 80°C. Signifikante skilnader vart ikkje påvist

ved Kappa-tal, men autoklavkokinga gav ein sterk indikasjon på at basing ved særs høg temperatur kan endre veden i flisa kjemisk, truleg ved ligninkondensasjon. I simuleringsforsøket oppnådde det basa derivatkoket høgare Kappa og lægre viskositet, medan silutskotet var 1/3 av silutskot utan basing.

Det vart konkludert med at basing vil gagne prosessen hjå Borregaard, men berre såframt basinga vert rett utført. Ein kombinasjon av rå flis med temperatur over 100°C og kald kokevæske vil gje betra impregnering. På den andre sida vil basing ved høge temperaturar truleg ha konsekvensar med tanke på ligninkondensasjon.

Introduction

Borregaard Industries Ltd. produces acid sulphite pulp in a wide range of qualities from Norway Spruce, (*Picea Abies* (L) Karst.). These pulps are mainly used as raw materials in the manufacture of cellulose derivatives such as cellulose ethers, esters, nitrocellulose and viscose, as well as for microcrystalline cellulose. One important feature in production of some qualities is to obtain a specific length of the cellulose molecule, normally measured as viscosity or named as degree of polymerisation (DP). Another feature is to maximise yield.

Production of the highest DP qualities is achieved by derivate cooking, a pulping process where reactivity parameters such as temperature and pressure are kept at a lower level than in the ordinary dissolving process. An unintentionally by-product is substantial quantities of uncooked wood chip cores. What could have been valuable pulp, is converted to reject, worthless to the factory.

1.1 Background

Several internal documents at Borregaard suggested that the reject was caused by problems in the front-end operation, and especially the phase of pre-steaming.

1.1.1 Front end of sulphite pulping

The front-end of cooking, starts by chipping debarked logs to wood chips. The chips are screened for over-thick chips and small sticks, achieving a uniform distribution and evenly cooked chips. To allow organic break down of resin structures in the wood, or simply just for storing, chips are kept in stock up to six weeks. Alternatively, chips are ripened in a silo for two days. Further, the chips are poured into the digester, and then steamed with saturated steam. This is the phase of pre-steaming.

Finally, the chips are flooded with sulphite liquor; a blend of limestone and water, reacted with sulphur dioxide. The fluid impregnates the wood, and the chemical separation of cellulose, hemicelluloses and lignin can begin.

1.1.2 Impregnation

Effective mass transfer of reactive chemicals into wood chips is of outmost importance for chemical pulping processes (MALKOV, TIKKA & GULLICHSEN 2001(**b**). Effective impregnation enables uniform pulping and reduced cooking time (GUSTAFSSON et al 1988, GULLICHSEN & SUNDQVIST 1995). Incomplete impregnation will, on the other hand, produce a large amount of uncooked cores of wood chips (Figure 1.1). According to STONE & FÖRDERREUTHER (1956), transport of reactive chemicals into the vessels of the wood chips is accomplished by two primary mechanisms: liquor penetration and diffusion. Liquor penetration refers to the flow of liquor into the air-filled voids of the wood chip under the pressure gradient. Diffusion refers to the movement of ions or other soluble matter through liquid, under the influence of the concentration gradient.



Figure 1.1: A sketch of a chip illustrating the effects of improper impregnation. Uniformity in pulp is not achieved; illustrated by Kappa number, a measure for content of lignin in the pulp.

In attempts of modelling the impregnation processes, impregnation is often considered as a diffusion-reaction process and complete penetration of the chip is assumed (MALKOV, TIKKA & GULLICHSEN, 2001(**a**) refers to EDWARDES, 1921 and SAUNDERSON & MASS, 1934). The reject at Borregaard suggests differently. Cooking liquor has not penetrated to the core of the chip.

1.1.3 Penetration research

Different techniques and methods have been used to obtain quantitative and qualitative information about the penetration process. Recording the time for oven-dry and treated

wood blocks to sink in water was one method of obtaining knowledge of penetration (STAMM, 1953 and STONE, 1956). With these methods, it was difficult to achieve reproducible and accurate results, due to a number of drawbacks and specific features of these procedures. Studying permeability, techniques where liquid is forced to penetrate different types of wood using special penetration clamps, have been useful. (STONE & GREEN, 1959, BANKS, 1970). Image analysis techniques, digitising and analysing photographs of sliced frozen chips after impregnation, has also been used for quantitative studies (JIMENEZ et al., 1990). In these methods there is a problem with interference between diffusion and penetration, and only a rough estimation of the penetration degree could be achieved with this method. Direct methods where various types of wood chips were treated with steam, measuring change in weight has provided more reliable information of penetration rates (MALKOV, TIKKA & GULLICHSEN 2001(b)). While the above-mentioned methods gives an estimation of the amount of penetrated liquid and the penetration rate, others provide qualitative information about the ways that liquid penetrate into wood voids. These methods include treatment of wood samples with liquid under controlled conditions, followed by microtoming and analysis (JENSEN et al., 1960, SAHAREH et al., 1995, OLSSON et al., 2001). Scanning electron microscopy (SEM) (OLSSON et al, 2001), staining and precipitation techniques (STONE, 1956) followed by microscopic observations as well as a radioactive tracer technique (JENSEN et al., 1960) are common methods for qualitative studies of penetration.

1.1.4 Factors affecting penetration

Results from research above, suggest organisation of the penetration process into three groups (Figure 1.2). The first group includes factors related to wood chips, such as structure of wood capillaries, the chemical composition of wood, the moisture and air contents of the chips, and chip dimensions. The second group includes factors related to the liquid, such as its viscosity, surface tension, composition, air solubility and air saturation degree. Process conditions, such as pressure, temperature and duration of penetration, form the third group of factors.



Figure 1.2: Factors affecting penetration of liquid into wood chips.

Air saturation

It is generally agreed that the air present within the wood capillaries is the main obstacle to rapid penetration of liquor (STAMM, 1953 and WOODS 1956). When penetration is allowed to occur from both sides of the wood chip, the backpressure of trapped air, which becomes compressed by capillary forces, soon checks the penetration (RYDHOLM, 1965). To reach a degree of penetration it is favourable to have chips with a high moisture content, and less air.

1.1.5 Pre-steaming

Pre-steaming during heating is a common technique for air removal from the wood chips. A flow of steam at atmospheric or super-atmospheric pressure causes thermal expansion of the trapped air, and a partial removal of air. However, the main effect on air removal is due to the increased pressure of water vapour, which causes air to be expelled from the chip (MALKOV, TIKKA & GULLICHSEN, 2001(a) refers to NOVIKOV et al., 1991 and ZORIN et al., 1970). Theoretically, complete air removal can be achieved when the partial pressure of water vapour inside the chip is equal to the ambient pressure. In addition to its primary objective of air removal, pre-steaming seems to improve the penetration process by affecting the structure of wood capillaries (MATSUMURA et al., 1999, NICHOLAS & THOMAS, 1968 and BAMBER & JOHNSTONE, 1968).

1.1.6 Factors affecting efficiency of pre-steaming

Important factors in pre-steaming are steaming temperature, pressure and time. An increase in steam temperature or pressure enhances the penetration rate of liquids (WOODS 1956). Even more critical than pre-steaming temperature is the duration of pre-steaming (RYDHOLM, 1965). Incomplete removal of air during pre-steaming is not necessarily related to low efficiency in heating, but can be caused by pressure resistance inside the wood capillaries. To achieve efficient steaming, it is important that the retention time is long enough for air to escape, and that the pressure-temperature relationship is correct (MALKOV, TIKKA & GULLICHSEN, 2001(**a**)).

1.2 Findings at Borregaard

Suspecting problems with pre-steaming, studies of the process revealed that pre-steaming was done at temperatures well below the boiling point (Figure 1.3). Except from heating, the main effect of these conditions would be some thermal expansion of air in the wood chips. Another effect could be condensation of steam on the chip surface.

On this basis, Borregaard initiated experiments on the effects of pre-steaming at temperatures above 100 C on pulp production and pulp properties. The results from experiments conducted in laboratories at Prosessindustriens Forskningsinstitutt (PFI), and

factory level at Borregaard, suggested that pre-steaming could have a positive effect on penetration, but assumed that the effect, if any, probably was reduced by condensate water diluting the cooking liquor (Borregaard, 1999). It was also observed a lowering of viscosity in cellulose, and a tendency of higher kappa numbers. The conclusion was that pre-steaming at Borregaard could be more harmful than beneficiary (Borregaard, 1999).



Figure 1.3: Computer image of a typical cook at Borregaard, Y/X-axis: Temperature and Time respectively. The vertical arrows indicate the phase of heating and pre-steaming; the area between the horizontal arrows is a full cooking cycle. The green line indicates that the process of pre-steaming occurs at temperatures between 60 and 80 °C.

1.3 The problem

GUSTAFSSON et al. (1988) and GULLICHSEN et al. (1995) state that more effective penetration of reactive chemicals into the core of the wood chip would:

- 1. Lower the temperature profile during cooking, leading to a lower process pressure
- 2. Increase batch capacity
- 3. Shorten batch cycles and achieve higher pulp production
- 4. Produce more uniform pulp

The Borregaard observations are supported by theory regarding the problem of uncooked cores, stating it is largely caused by improper impregnation, with special emphasis on penetration. The controversy is whether pre-steaming is beneficiary, or even harmful to the production of high DP cellulose. Considering that most of the chemical pulping industry makes use of this technique as an integrated process of their production, the findings cannot be left standing without further investigation.

1.4 Objectives

The objectives of this paper are to discuss the process and effects of chip pre-steaming. Divided in the following sub-objectives, the paper aims at:

- Study the technique of pre-steaming;
- Evaluate the factors and involved mechanisms by use of a pilot laboratory digester.

Method & Material

2.1 Structure

Based on the objectives, theory and findings, it was decided to conduct three different experiments, as indicated in Figure 2.1. Experiment A will test the effects of temperature and duration during pre-steaming, and phase of impregnation. Response is weight change, establishing how the factors are interconnected. Experiment B will use the same raw material and test for one response: Kappa number. Experiment C is the product of both A and B, simulating the normal batch cooking process. In the following, each experiment is handled separately.



Figure 2.1: The three experiments represented by colour. Raw material in green, factors in white, equipment in red, type of process in grey and response in yellow.

2.2 Data analysis

Experiments A and B were analysed using JMP statistical software. The minimum level of significance was set at p = 0.05.

2.3 Experiment A: Screening for effects of temperature and duration

2.3.1 Experimental design

The factors with corresponding levels (Table 2.1) were set up in a full factorial design of $2 \ge 3 \ge 2 = 24$, to screen the contribution of each factor on change in degree of liquor penetration. The runs were randomised and replicated once, giving a total of $2 \ge 24 = 48$ runs.

Experimental design for pre-steaming and impregnation trials					
Fac	tors	Levels			
Steaming	time, min	1	0		20
Steaming ten	nperature, ° C	80	105		120
Liquor temp	perature, ° C	5	50	•	80
Impregnatio	on time, min	1	0		20
Pattern	Steaming time	Steaming	Impregnation	time Lie	quor temperature
		temperature			
1111	10	80	10		50
1112	10	80	10		80
1121	10	80	20		50
1122	10	80	20		80
1211	10	105	10		50
1212	10	105	10		80
1221	10	105	20		50
1222	10	105	20		80
1311	10	120	10		50
1312	10	120	10		80
1321	10	120	20		50
1322	10	120	20		80
2111	20	80	10		50
2112	20	80	10		80
2121	20	80	20		50
2122	20	80	20		80
2211	20	105	10		50
2212	20	105	10		80
2221	20	105	20		50
2222	20	105	20		80
2311	20	120	10		50
2312	20	120	10		80
2321	20	120	20		50
2322	20	120	20		80

 Table 2-1: Experimental design. Water impregnation factors and levels.

2.3.2 Raw material

In February 2003 approximately 400 kg of fresh sawmill wood chips originating from Are Bruk was collected at Opsund chip silo, Borregaard. The chips were screened mechanically, sorted in 5 fractions, allowing the middle fraction between 2 to 6 mm's thicknesses to be retained. Details are described in SCAN CM 40:88.

The accept fraction was packed in 48 airtight polyethylene bags, 5 kg in each bag. To minimize moisture losses and to prevent biological degradation, the bags were frozen at 24°C in Stabburet AS food storage at Råbekken. As formation of ice crystals in the chip samples would block the liquor penetration into the wood matrix, the bags were collected three days prior to the experiments and defrosted at room temperature.

Basic density and dry matter content

Prior to freezing, a 200 g sample from each bag was taken to determine dry matter content (DMC), volume and density in the chips. DMC was determined according to SCAN CM 39:94, drying to constant weight at 105°C and 24 hours, calculated as in Eq. 1 below.

(Eq. 1)
$$DMC = \frac{m_b - m_a}{m_c - m_a} \times f$$

where: m_a is mass of box contain the sample, m_b is mass matter after drying, m_c is mass of sample, f is the factor where f = 100 gives DMC in % and f = 1000 is DMC in g/kg.

Basic density (ρ_{chip}) was determined as described in SCAN CM 43:89, where raw volume (ν_r) is measured as buoyancy (Eq. 2), dipping it completely in water and record change in weight of the water filled container. Properties are given in Table 2.2 below.

(Eq. 2)
$$\rho_{chip} = \frac{m_b}{v_r}, \quad \text{g/cm}^3$$

Wood chips – pre-steaming and impregnation trials						
Quality	Sawmill chips	Standard Deviation				
Basic density, g /cm ³	0.43	0.0120064				
Dry-matter content, %	58.2	5.0884754				

Table 2.2: Properties of the wood chips used in experiment A.

2.3.3 Equipment

The pilot recycle digester system (Figure 2.2), used both in Experiment A and Experiment C, is designed to simulate industrial cooking procedures at realistic temperatures, pressures and industrial time distributions of flows and concentrations. Equipped with several pipes for inlet and outlet fluids through top and bottom of the vessel, reversible flows, capability of cooking procedures up to 200°C and 30 bar pressure, it can simulate all known batch-cooking procedures.



Figure 2.2: To the left is a basic sketch of the experimental set-up, to the right a picture of the laboratory digester.

The heart of the system, the reactor, is equipped with a perforated container of approximately 15 litres, containing the material to be treated. Superheated steam can be

delivered to the system through the top lid of the vessel at temperatures up to 135 °C. Heating of fluid and control of liquor temperature is done recycling the liquor through an external heater. Temperature is maintained using a temperature sensor in the heater connected to the computer programme (Figure 2.3). Pressure can be manipulated by inlet of pressurised $N_{2(g)}$. Two temperature indicators located at top and bottom of the reactor monitor the temperature profiles in the vessel.



Figure 2.3: The system is fully instrumented for data logging and control, equipped with a control screen displaying a flow diagram for overview and control. Regarding flows, temperatures and pressures, clicking on the icons of equipment in question performed all adjustments.

2.3.4 Experimental procedure

The experimental phases were:

- **1. Preparations**: Wood chips were filled into the perforated container and weight recorded.
- 2. **Pre-steaming:** Saturated steam was let into the reactor, wood chips were heated and air removed.
- **3. Impregnation:** Pre-heated tap water from the accumulator tank was injected into the vessel. The water filled vessel remained at atmospheric pressure for the desired period.
- **4.** Recording of weight: The vessel was emptied of water, container removed, and weight recorded.

Preparations

A perforated container was hand-packed with 2 kg dry matter content of wood chips. Control of possible losses of moisture during storing was done by determination of DMC as described previously. Weight of container and chips (m_{start}), was recorded on an industrial scale of 5 grams accuracy. The container was placed in the reactor vessel and the lid tightened.

Pre-steaming

The bottom valve in the vessel was left open during steaming, allowing condensate and steam to flow out. Steaming time was recorded from the point both temperature indicators at top and bottom of the reactor showed the desired experimental temperature, in all cases less than a minute after initiating the sequence. At the end of pre-steaming, supply of steam was stopped and bottom valve closed.

Impregnation

Pre-heated tap water from the electrically heated accumulator was injected through the bottom of the vessel. Injection was done pressurising the accumulator tank with $N_{2(g)}$ at 2 bar. An open value at top of the vessel prevented a build up of pressure during injection

and the impregnation sequence. Injection lasted until water flowed out of the top valve, 2 minutes after initiation. At this point the vessel was full, and recording of impregnation time initiated. At end of impregnation, the bottom valve was opened and water let out, pressurised by $N_{2 (g)}$.

Recording of weight

Weight of the perforated basket and impregnated chips (m_{end}), was recorded 2 ½ minutes after impregnation was ended, time used to open the reactor and allowing free water to drip off the chips. Net change (Δm) was calculated as in Eq. 3 below:

(Eq. 3)
$$\Delta m = (m_{end} - m_{start})$$

2.4 Experiment B: Derivate cooking in autoclaves

2.4.1 Experimental design

Dry wood chips from Experiment A were cooked according to a standard derivate cooking programme (Table 2.7, Experiment C) in an autoclave laboratory digester. The product was analysed for possible effects of pre-steaming on lignin condensation. A capacity of 8 autoclaves in each batch, two of them to be used as reference, required a randomised design of 4 batches/blocks (Table 2.3).

Experimental design for autoclave cooking							
Autoclave	Batch 1	Batch 2	Batch 3	Batch 4			
A	1122	Reference	2312	Reference			
B	Reference	1121	2122	2111			
C	2311	Reference	1111	1222			
D	1221	2222	2211	1112			
E	2121	2322	Reference	Reference			
F	Reference	1321	1211	2212			
G	1212	1322	2221	2112			
Н Н	1311	1312	Reference	2321			

 Table 2.3: Experimental design for derivate cooking of dry treated wood chips from experiment A.

2.4.2 Raw material

Treated chips

Wood chips in Experiment A were cooled down and placed on separate marked cellulose sheets to air dry. After a week the dry chips were packed in separate polyethylene bags and stored at room temperature until Experiment B was initiated. For reference, a bag of the untreated, original sawmill chips was collected from storage at Råbekk and air-dried.

Cooking liquor

The sulphite cooking liquor to be used was a calcium bisulphite solution (Table 2.4). Derivate cooking liquor was prepared in a Duran bottle by mixing 150,5 g $Ca(OH)_{2(s)}$ and

tap water at 20°C to a 10,0 l solution. Pressurised $SO_{2(g)}$ was bubbled through a tube from the bottom of the bottle until all Ca(OH)₂ was dissolved. The method is described in TAPPI T 604 cm-85.

Table 2.4: Properties of cooking liquor used in experiment B. Total SO₂ expresses all sulphite ions present, while combined SO₂ is designated bound as monosulphite. Both components are expressed as percent of the solution. For example, 8% total SO₂ corresponds to a concentration of 80g/l.

Sulphite cooking liquor, CaO base			
Components	Derivate liquor		
Combined SO ₂	1,3 %		
Total SO ₂ :	8,0 %		

The sulphite cooking liquor is highly sensitive to $SO_{2(g)}$ fluctuation, making it necessary to prepare cooking liquor for each batch. Further, the concentration of SO_2 in the liquor is important for the delignification process and concentration has to be the same in every experiment. Concentration of total and combined SO_2 was verified according to internal Borregaard standards.

2.4.3 Equipment

In experiment B a laboratory autoclave digester was used to carry out the derivate cooking procedure. The automated system facilitates identical procedures.



Figure 2.4: Autoclave system; to the left: an autoclave with lid, middle: the cabinet with air fan below, and right: the rack where the autoclaves are mounted.

The cabinet, as shown in Figure 2.4 (above), has a capacity of 8 autoclaves, mounted on a vertically rotating rack, and temperature is logged with sensors pinned in the lids of every autoclave. The system is air heated by a large fan blowing hot air on the autoclaves. The system is fully automated, facilitating identical procedures. When cooking, all applications are controlled and monitored from a computer screen.

2.4.4 Experimental procedure

The experiments were performed according to internal Borregaard standards, conducted as described in the following.

- 1. Preparations: Prepare autoclaves and find dry matter content.
- 2. Cooking liquor: Production and analysis of cooking liquor to be used.
- 3. Evacuation: The autoclaves were evacuated and cooking liquor injected.
- 4. Cooking: Standard derivate cooking procedure.
- 5. Disintegration

Preparation

Eight stainless steel autoclaves marked A to H were used in the experiments. Each was filled with 210.0 g of air-dry chips, weight determined by a scale of 1/100 g accuracy. The two reference autoclaves were filled with air dry, untreated chips from the raw material as described in Experiment A. From the remaining chips in the polyethylene bags, a sample of 100 g was collected and %DMC determined according to SCAN CM 39:94.

Evacuating

The autoclaves were subject to 725 mm Hg vacuum (0.96 bar) for 1 hour, removing air from the autoclaves, facilitating impregnation of the chips. After filling, the autoclaves were placed in the preheated cabinet, and temperature loggers were mounted in each lid. The liquor-to-wood ratio, *LTW*, used was 4:1, referring to mass of dry matter. Volume of cooking liquor, V_{liquor} , was calculated as in Eq. 4 below.

(Eq. 4)
$$V_{liquor} = m_b \times LTW$$

Cooking

The chips were cooked according to parameters in Table 2.7, derivate cooking. The system was preheated to 65° before the 1st ramping was initiated. Interrupting the cooking was done placing the autoclaves in a water-cooled bench rack, cooling for 30 minutes.

Disintegration

Subsequent to cooling, the content of the autoclaves were emptied into plastic buckets and left in the cooking liquor for 8 hours at room temperature before disintegration. The procedure was performed according to standards for wet laboratory disintegration, ISO 5263:1995. Dry matter in pulp and reject was determined according to SCAN CM 40:88, the remaining pulp was granulated and packed in airtight polyethylene bags for further testing.

2.5 Experiment C: Cooking trials

2.5.1 Experimental design

Effects of pre-steaming on produced pulp examined cooking in the pilot laboratory reactor described in Experiment A, simulating the actual processes going on in the factory. Only four simulations were performed (Table 2.5). Factors were pre-treatment (pre-steaming or no pre-treatment) and cooking regime.

Experimental design for cooking simulations							
Block	Cooking regime	Pre-treatment					
1	Derivate, total/combined $SO_2 = (8.0/1.3)\%$	Yes					
1	Dissolve, total/combined $SO_2 = (8.0/0.9)\%$	No					
2	Derivate, total/combined $SO_2 = (8.0/1.3)\%$	No					
2	Dissolve, total/combined $SO_2 = (8.0/0.9)\%$	Yes					

Table 2.5: Full factorial blocked design of Experiment C.

2.5.2 Raw material

"Cell"quality chips

Chips of Norway Spruce (*Picea Abies* (L.) Karst.) were collected directly form the factory log chipper located at Opsund, Borregaard. The logs chipped were classified as "Cell", a low quality timber, stored for periods up to a year. Chips were screened according to the standard method SCAN-CM 40:88, packed and stored as in Experiment A.

Cooking liquor

Two types of sulphite cooking liquor was prepared with properties of derivate and dissolve liquor as stated in Table 2.6 below.

Sulphite cooking liquor, CaO base							
Components	Derivate liquor	Dissolve liquor					
Combined SO ₂	1,3 %	0,9%					
Total SO _{2:}	8,0 %	8,0%					

Table 2.6: Derivate and dissolve sulphite cooking liquors

Derivate liquor was prepared as in 2.4.4, experiment B, while properties of dissolving liquor was accomplished by reducing amount of Ca $(OH)_{2(s)}$ to 104.2 grams. Storing and analysis were as in Experiment B.

2.5.3 Equipment

The pilot laboratory digester is the same as described in Experiment A.

2.5.4 Experimental procedure

Preparations

For calculation of volume cooking liquor to be used, a sample to determine DMC was taken one day prior to the experiment. A wood to liquor ratio of 4:1 gave approximately 8,00 litres of fluid for the 2,00 kg DMC wood chips in the basket. The liquor was pumped into the heating accumulator and pre-heated to 65° C by circulating the liquor through the external heater. Two of the simulations required pre-steaming. This sequence was performed as in Experiment A, steaming for 15 minutes at 105° C. The cooking liquor was injected as soon as steaming sequence was to end, pressurising the accumulator tank with N₂. To prevent loosing cooking liquor, the top valve of the vessel was closed, building up an initial pressure of 2 bar prior to cooking sequence. This initial pressure was equal in 4 experiments.

Cooking

As soon as the cooking fluid was in the vessel, the bottom injection valve was closed, and circulation initiated. The liquor was pumped from the bottom of the vessel, through an external heater and injected at top, a constant downstream flow through all sequences of the simulation.

Cooking programmes, Experiment C							
Sequence	Derivate (Expe	riment A & C)	Dissolve (Experiment C)				
	Time	Temperature, °C	Time	Temperature, °C			
1st Ramp	180 minutes	65-105	180 minutes	65-105			
Sulphonation	60 minutes	105	60 minutes	105			
2 nd Ramp	180 minutes	105-128	180 minutes	105-145			
Time at temperature	180 minutes	128	90 minutes	145			

Table 2.7: Derivate and dissolve parameters



Figure 2.5: A graphical view of temperature development over hours, cooking programs

Cooling

At end of programme, cooling down the system was accomplished by water-cooling the reactor trough built in pipes, and by recycling the liquor through external liquor cooler. It took approximately 25 minutes to cool the reactor from 145°C to 25°C and 20 minutes for 128°C

Disintegration

The cold, spent liquor was collected in a bucked together with the pulped chips and left under lid overnight. Disintegration was performed according to standards for wet laboratory disintegration, ISO 5263:1995, and mass of pulp and reject calculated. Dry matter in pulp and reject was determined according to SCAN CM 40:88, the remaining pulp was granulated and packed in polyethylene bags for further testing.

The pulp was analysed for

- Kappa number in a laboratory analyser, Kappa Mat, complying with standards in SCAN-C 1:77.
- Viscosity according to internal standard. Derivate samples were bleached in order to measure the viscosity.

Results & Discussion

Results from Experiment A are based on the main 24 runs and the replicate, a total of 48 runs. Results from Experiment B contain only data from the first 24 runs, as a replicate was not conducted. Data tables for Experiments A and B can be found in Annex A.

3.1 Presteaming experiments

The impact of steaming temperature, steaming time, liquor temperature and impregnation time on weight change and Kappa number was screened using one-way analysis of variance (ANOVA). The overall results regarding statistical significance were poor, finding significance for steaming temperature and liquor temperature on net change only. However, factor profiles for the data were developed, enabling to check for trends in the data. The factor profiles are means of data for each level in each factor. These figures will be used, in addition to the standard significance tests, to shed light on the objectives and problems stated in the introduction. Figure 3.1 and 3.2 show factor profiles, stippled lines indicate level and combination of factors to maximise the response.



Figure 3.1: Best combination to maximise net change (kg), data means for other levels. 95 % confidence intervals for means of observations indicated by vertical line in all levels.



Figure 3.2: The combination giving the highest Kappa number is indicated, data means for other levels. 95 % confidence intervals for means of observations indicated by vertical line in all levels.

3.1.1 Net change - effects of duration

The analysis shows no significant effects of steaming time and impregnation time on the net change in weight (Table 3.1). However, when increasing the duration from level one to two, steaming and impregnation sequences both show a trend of slightly higher values (Figure 3.1). Although not significant, the profiles show similarity to results in other experiments (MALKOV, TIKKA & GULLICHSEN, 2001 (b) and (c)). The longer the time, the further the process goes. In this experiment most of the impregnation seems to have occurred at point of level 1 = 10 minutes.

Table 5.1: Concrence (One-way ANOVA) between net change (kg) and durat	ratior
--	--------

Factor	Response	DF	RMSE	\mathbf{R}^2	F Ratio	Prob > F
Steaming time	Net change	1,46	0.178508	0.023843	1.1236	0.2947
Impregnation	Net change	1,46	0.18012	0.006135	0.2840	0.5967
time						

Testing efficiency of penetration, the MALKOV, TIKKA & GULLICHSEN, 2001 (b) and (c) experiments show that more than 60 % of total impregnation occurs during the first 10

minutes, even at low temperatures and for most types of wood and coniferous species. Further, sapwood chips of all species shows considerably faster impregnation rates, than those of heartwood. Since the raw sawmill chips used in experiment A and B normally is produced from the outer layers of the stem, arguing that content of sapwood is a source of rapid impregnation stands to reason.

3.1.2 Kappa - effects of duration

Coming to Kappa numbers, no significant effect can be found increasing time from 10 to 20 minutes (Table 3.2).

Factor	Response	DF	RMSE	\mathbf{R}^2	F Ratio	Prob > F
Steaming time	Kappa	2,27	3.502296	0.064103	0.9247	0.4089
Impregnation	Kappa	2,27	3.520013	0.05461	0.7798	0.4685
time						

Table 3.2: Coherence (One-way ANOVA) between Kappa number and duration

3.1.3 Net change - effects of temperature

Steaming temperature

Analysis on a 95 % confidence interval using Student's t test for each pair, shows significant difference for net change in weight for 80 °C and 105 °C steaming temperature (Figure 3.3). However, Tukey Kramer test for all pairs, does not show significance for the same interval of confidence. The reason for this disagreement could be found in the data, as Tukey Kramer compares all pairs, and Students' t each pair, making Tukey Kramer a stricter "test". Unusual observations could cause this, but it has not been possible to isolate and exclude any of the observations. Neither of the tests shows significant difference for 120°C.



Figure 3.3: Significance of levels (One-way ANOVA). Level 1 and 2 are significantly different using Student's t (different colour of rings). Tukey Kramer does not show significance.

Table 3.3: Coherence (One-way ANOVA) between net change (kg) and steaming temperature (°C)

Factor	Response	DF	RMSE	\mathbf{R}^2	F Ratio	Prob > F
Steaming	Net change	2,45	0.170851	0.125234	3.2212	0.0493
temperature						

It can be concluded that there is an apparent difference when steaming over and under the boiling point of water, and that the difference probably is significant.

Further, studying the factor profile in Figure 3.1, data means for net weight change at 105°C and 120°C show less for the latter. This result can be explained by the combination of hot impregnation liquor and high temperature in the chips and chip-heating environment. Adding cooking liquor at 80°C to a system where both wood chips and a massive steel vessel hold 120°C, would, with the volumes of 15 litres liquor, bring the net temperature to 100°C or more. At atmospheric pressure, as conditions were in experiment A, this would cause the system to boil. Impregnation would go slow or stop until net temperature came under 100°C or over-pressure was applied. Although no significant values are found, the explanation is feasible.

Liquor temperature

temperature

Liquor temperature shows significance for both confidence tests (Figure 3.4 and Table 3.4). A low temperature of liquor seems to induce a higher degree of penetration.



Figure 3.4: Significance of levels (One-way ANOVA). Level 1 and 2 are significantly different using Student's t and Tukey Kramer test at 95 % interval of confidence (different colour of rings).

Higher temperature gives lower impregnation. These observations are in accordance with the theories given of RYDHOLM (1965); pre-steaming causes moisture in the wood cells to evaporate, forcing air out of the chip. Adding cold liquor would cause a vacuum in the voids, sucking liquor into the wood matrix. The difference in temperature between steam in wood voids and liquor, is a probable explanation.

temperature (°C)							
Factor	Response	DF	RMSE	\mathbf{R}^2	F Ratio	Prob > F	
Liquor	Net change	1,46	0.17302	0.08294	4.1603	0.0471	

Table 3.4: Coherence (One-way ANOVA) between net change (kg) and liquor temperature (°C)

3.1.4 Kappa - effects of temperature

Analysing for significance at a 95 % interval of confidence did not establish significant differences, neither for steaming temperature nor liquor temperature. Figure 3.5 and Table 3.5 show significance and coherence between steaming temperature and Kappa number.



Figure 3.5: Kappa number by steaming temperature. Level 0, Kappa number indicated by stars in the figure was the untreated reference. No significance established.

Figure 3.5 above shows that the greatest difference is between the reference and level 3, 120°C. The other levels are closer to the reference. Although significance is not present in the data, arguing that high temperature could affect the wood structure is plausible. RYDHOLM (1965), claiming that temperatures of 120°C could cause condensation of lignin, supports this argument.

 Table 3.5: Coherence (One-way ANOVA) between Kappa number and steaming temperature levels, and Kappa number and liquor temperature

Factor	Response	DF	RMSE	\mathbf{R}^2	F Ratio	Prob > F
Steaming	Kappa	3,26	3.473734	0.113405	1.1086	0.3635
temperature						
Liquor	Kappa	2,27	3.54055	0.043546	0.6146	0.5482
temperature						

Regarding liquor temperature (Table 3.5), there were no significances or trends observed.

3.2 Experiment C: Cooking simulations

Cooking simulations were carried out merely to test the Borregaard observations mentioned in the introduction, evaluating the pre-steaming experiments from the pulp point of view.

3.2.1 Properties of the pulp

For dissolving pulp, there are not apparent differences in the observations. Thus, it seems that the pre-steaming has little influence on the responses. Regarding derivate cooking, however, higher Kappa and lower viscosity was observed for pre-steaming. This is in line with the findings at Borregaard, as mentioned in the introduction. The difference in 8 units of Kappa is substantial. Viscosity is also different by 71 units, which also must be said to be substantial. Reject, on the other hand, is 3,5 times greater for derivate without pre-treatment. It seems that pre-steaming has actually improved the impregnation.

Block	Cooking regime	Pre-steam @ 105°C, 15 min	Kappa	Viscosity	Reject % of DMC
1	Derivate, total/combined SO ₂ = $(8.0/1.3)\%$	Yes	69	1448	0.8
2	Derivate, total/combined SO ₂ = $(8.0/1.3)\%$	No	61	1519	2.9
1	Dissolve, total/combined SO ₂ = $(8.0/0.9)\%$	No	10	919	0.2
2	Dissolve, total/combined SO ₂ = $(8.0/0.9)\%$	Yes	10	918	0.1

Table 3.6: Viscosity and Kappa -Experiment C

It must be added that only four trials were run, and of these, and only the two derivates were directly relevant for experiments A and B. But on the other hand, by conducting

only these two experiments, the Borregaard findings were illustrated by reject, Kappa number and viscosity.

3.3 A factorial view – errors in experiments

In the experimental designs there are many possible errors. The biggest source of error in these experiments was knowledge of how to use the laboratory digester and autoclave cabinet. Several pre-feasibility experiments were carried out in order learn the operation procedures and identify built-in sources of error. Since pre-steaming and impregnating are relatively easy and straightforward operations, the possible errors made should not overshadow the results.

3.3.1 Factors related to the wood

The most important factor that affects the penetration is the capillary structure of wood chips. The structure of the wood capillaries, defined by their types, geometry, distribution and accessibility, is different in softwoods and hardwoods, sapwood and heartwood, early wood, latewood, normal wood and reaction wood. It also varies between wood species.

With relevance to the conducted experiments, only the species and its factory decided sorting quality, "sawmill" and "cell wood", was known. In many fields of research such a selection of material would be considered as a cause of error in the data. On the other hand the method of material selection used in this paper requires nothing but uniformity in quality and comparability. The wood chips used should possess the same qualities as in the production. Consequently, focus has been on keeping the raw material in a comparable condition. From this point of view it can be argued that obtaining significant data from the industrial raw material makes the method more robust. There is also a possibility that this is one reason for not finding clearer significance in the data.

3.3.2 Factors related to liquid

The chemical composition of the penetrating liquid may affect the penetration process. In Experiment A, only tap water was used. Using water was deliberate, and avoided other impacts than of the factors studied.

The cooking liquor used in Experiment B and C opened for errors. It was difficult to achieve the same concentration of combined SO₂ from one experiment to the next. The viscosity of the penetrating liquid and the surface tension at the liquid-gas interface are major characteristics influencing the flow rate in wood and the capillary rise (RYDHOLM, 1965). Further, solubility of air in the penetrating liquid and the degree of air saturation at the beginning of penetration, determine the efficiency of the final penetration phase (MALKOV, TIKKA & GULLICHSEN, 2001(**a**)). Small differences in composition would mostly affect the penetration, but first of all the cooking process. Errors in chemicals present in the penetrating liquor may also alter the capillary structure of the chip. However, there were not recorded any block effects in the experiments.

Conclusion

In these three experiments attempts have been made to illustrate and investigate the possibilities and constraints regarding pre-steaming.

The problems to be addressed were visualised with Experiment C, producing the same results as the initial findings at Borregaard; a high Kappa number and lower viscosity. The experiment also illustrated the benefits of pre-steaming, reducing the amount of reject.

Experiment A verified significant effects of liquor temperature and steaming temperature. The effect is caused by difference in temperature, probably most effective if the chips hold a temperature above 100°C and cold liquor is added. On this basis it can be concluded that pre-steaming is an effective technique to achieve a higher degree of liquor penetration.

However, Experiment B spotted a possible constraint of steaming at high temperature. Trends indicate that high temperatures during steaming could cause higher Kappa number. Condensation of lignin in the wood is a known phenomenon in high temperature drying applications; this could also be the fact for pre-steaming.

Based on the experiment results, this study establishes pre-steaming as an effective technique to achieve a higher degree of penetration in wood chips. On the other hand, it could seem that pre-steaming has undesirable effects on Kappa and viscosity. The experiments show that factors like steaming temperature and liquor temperature are important, and improving these parameters would improve pre-steaming at Borregaard. However, at Borregaard, optimal pre-steaming conditions are difficult to obtain, as steam is added directly to the 120-ton capacity batch boilers. A separate pre-steaming stage, similar to pre-steaming in continuous Kraft cooking processes, could be a solution.

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Annex A

Pattern	Steaming time	Steaming	Liquor	Impregnation	Net change, kg	Kappa number
		temperature	temperature	time		
Reference	0	0	0	0	•	32.2
Reference	0	0	0	0	•	36.9
Reference	0	0	0	0	•	36.6
Reference	0	0	0	0		34.6
Reference	0	0	0	0		33.5
Reference	0	0	0	0		36.2
-0	1	2	1	1	1.37	39.7
-0	1	2	1	1	1.495	
-0-+	1	2	1	2	1.455	
-0-+	1	2	1	2	1.46	38.1
-0+-	1	2	2	1	1.255	36.9
-0+-	1	2	2	1	1.41	
-0++	1	2	2	2	0.845	31.3
-0++	1	2	2	2	1.32	
	1	1	1	1	1.12	
	1	1	1	1	1.195	31
+	1	1	1	2	1.07	
+	1	1	1	2	1.465	42.1
+-	1	1	2	1	1.04	
+-	1	1	2	1	1.505	39.5
++	1	1	2	2	1 13	0710
++	1	1	2	2	1.13	35
	1	3	1	1	1 385	55
	1	3	1	1	1.505	
	1	3	1	2	1.31	51.1
	1	3	1	2	1.373	
	1	3	2	2	1.455	26.4
-++-	1	3	2	1	1.00	30.4
-++-	1	3	2	1	1.44	
-+++	1	3	2	2	1.25	39.4
-+++	1	3	2	2	1.44	
+0	2	2	1	1	1.41	
+0	2	2	1	1	1.45	31.8
+0-+	2	2	1	2	1.38	37.5
+0-+	2	2	1	2	1.58	
+0+-	2	2	2	1	1.19	40.4
+0+-	2	2	2	1	1.52	
+0++	2	2	2	2	1.435	33.1
+0++	2	2	2	2	1.52	
+	1	1	1	1	1.15	35.8
+	2	1	1	1	1.47	
++	2	1	1	2	1.085	34.1
++	2	1	1	2	1.3	
+-+-	2	1	2	1	0.985	
+-+-	2	1	2	1	1.28	32.9
+_++	2	1	2	2	1.25	36.7
+_++	2	1	2	2	1.48	
++	2	3	1	1	1.35	
++	2	3	1	1	1.535	43.6
++-+	2	3	1	2	1.445	30.3
++-+	2	3	1	2	1.47	
+++-	2	3	2	1	0.895	40.5
+++-	2	3	2	1	1.385	
++++	2	3	2	2	1.255	36
++++	2	3	2	2	1.4	
L	I	l		1	1	1

Table A: Experimental data for Experiment A and B. Data sorted by pattern (paired main and replicate)