DIGESTIBILITY AND PAPER-MAKING PROPERTIES OF PREHYDROLYZED SOFTWOOD CHIPS

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The effect of hemicellulose extraction of pine wood chips by water prehydrolysis on subsequent kraft cooking and paper properties was studied. Prehydrolysis reduced the required cooking time by approximately 40% and increased kappa number reduction in oxygen delignification. Prehydrolysis decreased the overall brownstock pulp yield on wood by 7.2 percentage units. Consequently, valuable products would need to be produced from the prehydrolyzate to compensate for the resulting increase in wood consumption. In DED-bleaching, lower bleaching chemical dosages were needed with prehydrolyzed than with unhydrolyzed pulps to obtain similar final brightness. As expected, removal of hemicelluloses led to a decrease in the tensile index and increase in the tear index. At a given density, the strength potential of prehydrolyzed pulps was higher than that of unhydrolyzed pulps. There was an up to more than fivefold increase in beating revolutions in a PFI-mill needed to obtain comparable tensile indices. This significant reduction in beating response might pose problems in the commercialization of prehydrolyzed pulps. In general, differences between the paper properties of prehydrolyzed pulps and unhydrolyzed pulps are attributed to decreased inter-fiber bonding in prehydrolyzed pulps.

Keywords: Water prehydrolysis; Cooking; Bleaching; Beating; Paper-making properties

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INTRODUCTION

The finite nature of fossil fuels and their contribution to carbon dioxide emissions have motivated increasing interest in biofuels. This, in turn, has led to the development of various biorefinery concepts (see, e.g. Kamm and Kamm 2004) in which biomass is converted to biomaterials and biofuels in fully integrated systems. Existing forest industry facilities could play a key role in the utilization of ligno-cellulosic biomass, as the people who run such facilities already possess the know-how, logistics, and infrastructure for procuring, transporting and processing lignocellulosics. Thus, different biorefinery concepts aimed at combining biofuel production with pulp and paper production have attracted interest in academia and industry. These concepts can be called, e.g., integrated forest biorefineries (IFBR) (van Heiningen 2006).

One option to convert a pulp mill into a pulp and biofuels and/or biochemicals producing biorefinery would involve the extraction of hemicelluloses from wood chips. As a steam-phase prehydrolysis process, hemicellulose extraction is conventionally used in the production of high-purity dissolving pulps. Carried out in an aqueous phase, hemicellulose extraction could enable the extraction of valuable hemicelluloses prior to kraft paper pulp production. Hydrolyzation of hemicelluloses to monomeric sugars with fermentation to ethanol would enable the co-production of ethanol and pulp. An existing pulp mill in Old Town, Maine, USA, is currently being converted to a biorefinery utilizing hemicellulose extraction technology (Pendse *et al.* 2009). In addition to ethanol, other products and chemicals could also be produced from hemicelluloses, such as films and coatings (Hansen and Plackett 2008). The sugars formed in the hydrolysis of hemicelluloses could be used to produce various chemicals; a U.S. DOE study lists over 300 potential building block chemicals that could be produced from sugars and synthesis gas of biomass (Werpy et al. 2004).

The extraction of hemicelluloses from wood chips can be done prior to cooking in a so-called pre-extraction process. Several methods for the extraction of hemicelluloses have been reported. In a prehydrolysis process, the hemicelluloses are hydrolyzed to oligomeric and monomeric sugars with the aid of, for example, pressurized hot water (autohydrolysis) (e.g. Casebier et al. 1969; Garrote and Parajo 2002; Yoon et al. 2008; Al-Dajani et al. 2009; Leschinsky et al. 2009), dilute acids (e.g. Parajó et al. 1994; Frederick. et al 2008; Al-Dajani et al. 2009) or steam (e.g. San Martín et al. 1995). Hemicelluloses can also be extracted by alkaline extraction before (e.g. van Heiningen et al. 2008; Al-Dajani and Tschirner 2008) or even after pulping (Pekkala 2008).

When commercializing these hemicellulose pre-extraction processes, their effect on the kraft fiber line and on the papermaking properties of subsequent pulps is of key importance. The extraction of hemicelluloses has been reported to affect cooking (Sixta 2006a; Smith et al. 2008; Yoon and van Heiningen 2008; Al-Dajani et al. 2009), O_2-delignification (Antonsson et al. 2003; Sixta 2006b,c), hornification and swelling tendency (Oksanen et al. 1997; Moss and Pere 2006), beating response (Vaaler et al. 2002; Yoon and van Heiningen 2008), and strength properties (Spiegelberg 1966; Rydholm 1967; Kettunen et al. 1982; Molin and Teder 2002). Although several studies on the effect of hemicellulose extraction on various isolated aspects of fiber line and paper-making properties have been published, more comprehensive studies on the pulping and paper making properties of hemicellulose-extracted chips are lacking. Yoon and van Heiningen (2008) have studied the digestibility, beatability, and paper properties of hot-water prehydrolyzed loblolly pine (*Pinus Taeda*) chips. With the exception of Yoon and van Heingingen (2008), there appear to be no studies comprising the whole fiber line, including bleaching and testing of bleached sheets. There is therefore a need for a study examining the whole fiber line, from hemicelluloses extraction and cooking to testing of bleached pulps.

This paper is part of the *Biojalostamo Sellutehdas (BiSe)* project, studying the conversion of a conventional kraft pulp mill into a pulp and biofuel-producing biorefinery. It is continuation to a paper presented elsewhere (Kautto et al. 2010) in which the integration of a prehydrolysis bioethanol process to a kraft pulp mill was discussed. This paper discusses the effect of water prehydrolysis of pine wood chips on cooking, oxygen delignification, bleaching, beating, and paper properties.

EXPERIMENTAL

The cooking experiments were carried out in the Department of Forest Products Technology at Aalto University, School of Science and Technology. The pulp beating, bleaching, and papermaking property experiments were carried out at

NabLabs Oy, Rauma, Finland.

Materials

The wood raw material used was industrial pulp wood chips collected from a pulp mill located in South-East Finland. The raw material was mainly Scots pine (*Pinus Sylvestris*), and the sample possibly contained some amount of Norway spruce (*Picea Abies*). The industrial wood chips were screened (SCAN-CM 40:01). The accepts were the fraction passing 7 and 13 mm slot sizes. The fraction was then manually checked for knots and bark.

Methods

The experiments were carried out for an unhydrolyzed reference pulp (**pulp 1**) and for prehydrolyzed pulps cooked at sulfidity levels of 40% (**pulp 2**) and 20% (**pulp 3**). The reference pulp 1 was cooked at a sulfidity level of 40% and then bleached. Pulps 2 and 3 were first prehydrolyzed with hot water at 150 °C and then cooked and bleached.

Prehydrolysis at P-factor 200

Pulps 2 and 3 were prehydrolyzed with hot water for the extraction of hemicelluloses. In the prehydrolysis, 3000 g of pine wood chips were placed in a 20 liter digester. Deionized hydrolysis water was then introduced to the digester to obtain a liquor-to-wood ratio of 4.6 L/kg. The mixture was first heated to 80 °C, and then to 150 °C at a rate of 2 °C/min. The mixture was kept at 150 °C for 1 h 33 min. This corresponds to a P-factor of 200. The P-factor is a term representing the severity of a hot water hydrolysis treatment. The P-factor was calculated from the recorded temperature/time data according to Sixta (2006a), based on an activation energy of 125.6 kJ/mol. After the set time, a valve was opened at the bottom of the digester, and the hydrolysis liquor (prehydrolyzate) was drained from the digester. The wood chips were then cooked. There was no intermittent chip washing between prehydrolysis and cooking.

Cooking

The cooking was carried out in the same digester as used in the prehydrolysis. With pulps 2 and 3, the hydrolyzate was drained from the digester after prehydrolysis. With pulp 1, 3000 g of chips were placed in the digester. 1 liter of deionized water was introduced to the digester. The liquid-to-wood ratio was then adjusted to 4.6 by adding deionized water and cooking chemicals. The effective alkali (EA) level during cooking was 20%, expressed as NaOH based on oven dry wood, in all cooks. The sulfidity level was 40% for pulps 1 and 2 and 20% for pulp 3. The digester was first heated to 80 °C, and then to the cooking temperature of 160 °C at a rate of 1.5 °C/min. The cooking was stopped at an H-factor of 1600 in the case of the reference pulp. This H factor corresponded to a cooking time of 3 h 51 min. With pulp 2, the cooking was stopped at an H-factor of 1000 (cooking time of 2 h 22 min), and with pulp 3, the cooking was stopped at an H-factor of 1300 (3 h 6 min). Draining of the digester was started two minutes before the set cooking time. After the set cooking time had been reached and the digester had been drained, the digester was filled with NaOH solution (5 g/L). The mixture was then heated to 80 °C and kept at 80 °C for 10 minutes. It was subsequently drained, and the digester was filled with deionized water. The mixture was similarly heated to 80 °C and kept at 80 °C for 10 minutes.

After that, the water was drained and the NaOH solution treatment was repeated two times. The pulp was then removed from the digester, centrifuged, homogenized, and weighed. Its dry solids content was measured according to SCAN-C 3:78. The metal content of the pulps was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Screening

The pulps were first wet disintegrated and then screened with a TAP031 screener with a 0.25 mm slot size. The accepts fraction was then homogenized. The dry solids content of the accepts and rejects was then analyzed according to SCAN-C 3:78.

Bleaching

All pulps were oxygen delignified and subsequently bleached with a DED-sequence. Oxygen delignification was done for 600 gram pulp batches in a 16 litre rotating pressurized cooking apparatus. The count for the 30-minute reaction time started when the temperature of the cooking apparatus reached 89 °C. After oxygen delignification the pulps were washed three times with 12 litres of deionized water and homogenized for three minutes with a Tripas Planet kitchen mixer.

Unpressurized laboratory bleaching was carried for 300 gram pulp batches in plastic bags in a hot water bath. ClO_2 for the bleaching stage was acquired from a pulp mill located in Western Finland as a water solution. Appropriate safety measures were taken in handling the solution and the D bleaching stage (ventilated hood, safety goggles and mask etc.). Chemical charges used in the bleaching stages D_0 and E were calculated from the kappa number after O_2-delignification. Chemical charge in the D_1-stage was the same for every pulp batch. Pulps were washed two times with 60 litres of deionized water after the D_0- and D_1-stages and a similar procedure plus an additional wash with 20 litres of deionized water was applied after the E-stage. The oxygen delignification and bleaching conditions for all pulps are presented in Table 1.

Table 1. Oxygen Delignification and Bleaching Conditions with Chemical Charge Amounts

Sequence	**O**	**D_0**	**E**	**D_1**
Pulp consistency, %	10	10	10	10
Act. Cl charge %		0.2×incoming kappa		1
NaOH charge %	2		0.6×D_0 charge	
Temperature, °C	90	60	60	70
Time, min	30	45	75	180
Pressure, bar	5			
Target end pH		~2	~12	~3.6

Viscosity (ISO 5351-1:1981) of the pulp samples was measured after O_2-delignification and bleaching stages E and D_1. The ISO brightness (ISO 2470:1999) of the pulp samples was measured after O_2-delignification and bleaching stages E and D_1. Kappa numbers (ISO 302:2004) were determined before and after oxygen delignification.

Handsheet properties

The mechanical properties of the pulps were evaluated by handsheet testing (ISO 5270:1998). The pulps were refined in a PFI mill (ISO 5264-2:2002), handsheets were prepared (ISO 5269-1:1998) with different degrees of beating, and the CSF-values were measured (ISO 5267-2:2001).

RESULTS AND DISCUSSION

The Effect of Prehydrolysis on Cooking and Oxygen Delignification of Chips

Prehydrolysis of the wood chips was carried out at P-factor of 200 at 150 °C. For prehydrolyzed pulps 2 and 3 the hydrolyzate was then drained from the digester and the chips were cooked and oxygen delignified. With constant conditions in oxygen delignification, the target kappa number after O_2-delignification was 15 for all pulps. Based on earlier experiments on smaller scale laboratory digesters (presented in Kautto et al. 2010), it was assumed that prehydrolyzed chips can be cooked at lower H-factors and that they respond better to O_2-delignification. The cooking of prehydrolyzed chips was therefore carried out with lower H-factors, and the target kappa numbers after cooking were higher. Pulp 2 was cooked at an H-factor of 1000 at a sulfidity level of 40% and pulp 3 at an H-factor of 1300 at a sulfidity level of 20%. The reference chips (pulp 1) were cooked at an H-factor of 1600. Figure 1 presents the yields on wood and kappa numbers of prehydrolyzed and unhydrolyzed chips after cooking and O_2-delignification. Table 2 presents the yields on wood, kappa numbers, residual alkalis, viscosities, and ISO-brightnesses after cooking and O_2-delignification.

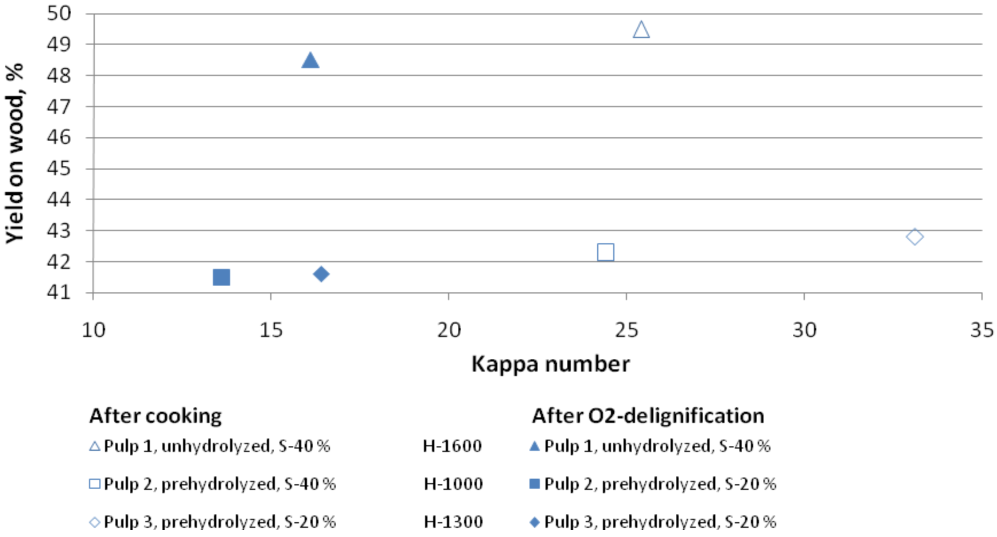

Fig. 1. Yield on wood versus kappa number after cooking and oxygen delignification of pulp 1 (unhydrolyzed reference chips cooked at a sulfidity of 40% at an H-factor of 1600) and pulps 2 and 3 (chips prehydrolyzed at a P-factor of 200 and cooked at an H-factor of 1000 and a sulfidity level of 40%, and at an H-factor of 1300 and a sulfidity level of 20%, respectively). Effective alkali level was 20% in all cooks.

Table 2. Yield on Wood, Kappa, Residual Alkali, and Viscosity after Cooking for Pulps 1, 2, and 3

	Cooking				O_2-delignification			
Pulp	Yield on wood, %	Kappa	Residual alkali, g/l	Viscosity, ml/g	Yield on wood, %	Kappa	ISO-brightness	Viscosity, ml/g
1	49.5	25.4	7.9	1280	48.5	16.1	37.7	1055
2	42.3	24.4	9.8	1320	41.5	13.6	42.5	1070
3	42.8	33.1	10.5	1280	41.6	16.4	39.4	1010

As can be seen in Fig. 1, at similar sulfidity levels of 40%, the H-factor can be lower with prehydrolyzed chips to obtain similar kappa numbers. The H-factors for reference and prehydrolyzed chips were 1600 and 1000, and kappa numbers after cooking were 25.4 and 24.4, respectively. With a cooking temperature of 160 °C and a heating rate of 1.5 °C/min, this would be equivalent to a shortening of the cooking time from 3 h 51 min to 2 h 22 min (39%). This is in line with the findings of Yoon and van Heiningen (2008), who report that with approximately 5% to 8% of wood material (loblolly pine) extracted during water prehydrolysis, the delignification rate constants in the subsequent kraft cooking are 40% to 60% higher than with unhydrolyzed chips. The lower required H-factors and higher delignification rates would imply that the digestibility of prehydrolyzed chips is higher. The enhanced delignification of prehydrolyzed chips has been attributed to improved permeability of the cell wall caused by increased pore volume, resulting in improved penetration of the cooking liquor, and hydrolytic cleavage of lignin structures and covalent bonds of lignin-carbohydrate complexes (LCC) during pre-extraction (Sixta 2006a). The shortened cooking time could potentially enable a capacity increase in cooking. Reducing the sulfidity level from 40% to 20% in cooking of prehydrolyzed chips (pulps 2 and 3) increases the required H-factor. As expected, the higher sulfidity level would therefore seem to increase the delignification rate in the cooking of prehydrolyzed chips.

As can be seen in Table 2, the yields on wood after cooking of pulps 1 and 2 are 49.5% and 42.3%, respectively. To obtain a similar brownstock pulp production, this 7.2 % percentage unit drop in yield on wood would signify an increase in wood consumption by approximately 17%. This is in agreement with our previous results (Kautto et al. 2010), where a 16% wood consumption increase was calculated based on smaller-scale prehydrolysis and cooking experiments. This would imply that potentially more valuable products than biofuels would need to be produced from at least part of the prehydrolyzate to compensate for the rather significant increase in wood consumption. The determination of the minimal values of the products produced from the prehydrolyzate requires careful economic analysis of the prehydrolysis process. A comprehensive economic analysis of the process is, however, beyond the scope of this study.

The composition of the hydrolyzate was not analyzed in this set of experiments. A thorough mass balance calculation of the prehydrolysis and cooking could not therefore be carried out. However, assuming that 14.1% of wood material (approximately 50% of which being carbohydrates) would be dissolved at P-factor 200 at a temperature of 150 °C as in our previous experiments (Kautto et al. 2010, note a smaller-scale digester, different temperature profile of prehydrolysis and a different set of raw material), the cooking yield of pulp 2 would be 49.2%. Taking into consideration that the kappa number after cooking was slightly lower with pulp 2, it would seem that the cooking yields of water prehydrolyzed and unhydrolyzed softwood pulps are rather similar. In the literature, prehydrolysis has however been reported to decrease the cooking yield. With 5.0% and 7.0% of loblolly pine pre-extracted in water prehydrolysis at 170 °C, Yoon and van Heiningen (2008) present the yields on wood after cooking to be approximately 42.5% and 39.5%. Based on these extraction amounts and pulp yields, and a yield of approximately 45.5 % of unhydrolyzed pulps at equal kappa numbers, the cooking yields can be calculated to be approximately 0.8 and 2.6 percentage units lower with prehydrolyzed chips. Similarly, cooking yield decreases of approximately 3 to 4% units can be calculated based on the results of Al-Dajani et al. (2009) where 19% of aspen wood was dissolved in water prehydrolysis at 150 °C for 4.5 h prior to cooking. It would therefore seem that pre-extraction of hemicelluloses prior to pulping either leads to degradation of carbohydrates that would be stable in conventional kraft pulping with no pre-extraction in the prehydrolysis stage, or it enhances such degradation in the cooking stage, thus lowering the cooking yield. Based on earlier experiments with a different reactor and a different batch of raw material, a slightly too high assumption of 14.1% of wood extracted in prehydrolysis could possibly explain the seemingly similar cooking yields of unhydrolyzed and prehydrolyzed chips found in this study.

Under constant conditions of oxygen delignification, kappa reduction was significantly higher with prehydrolyzed chips than with reference chips. The kappa number was reduced by approximately 37%, 44%, and 50% with pulps 1, 2, and 3, respectively. This improved response to O_2-delignification allows stopping of the cooking at higher kappa numbers with prehydrolyzed chips. The better response of prehydrolyzed chips to oxygen delignification has previously been shown for E. saligna hardwood chips (Sixta 2006b). The increased kappa reduction of hemicellulose-poor prehydrolyzed chips is also in line with the findings of Zou et al. (2002). By varying the xylan content of brownstock hardwood kraft pulp with the use of anthraquinone, they found that a higher amount of xylan decreases the rate of oxygen delignification. This would imply that the amount of xylan affects the accessibility of the chemical reactants in the O_2-stage. The higher kappa reduction of prehydrolyzed pulp 3 than that of prehydrolyzed pulp 2 could probably be explained by the higher kappa number before O_2-stage. It has been shown that a higher kappa number after softwood kraft cooking leads to a higher kappa number reduction in subsequent O_2-delignification (Poukka et al. 1999). Possibly, this is because pulps with higher kappa numbers after cooking contain a larger amount of easily removable lignin fragments. With low residual kappa numbers, pulps have been shown to contain relatively more LCCs that are difficult to delignify (Lawoko et al. 2004).

In addition to kappa number reduction, the response of pulps to O_2-delignification can also be characterized by selectivity. Selectivity is normally defined as the reduction of viscosity per kappa unit. Based on data presented in Table 2, the selectivities of pulps 1, 2, and 3 would be approximately 24.2, 23.1, and 16.2 (Δml/g)/Δkappa, respectively. The selectivity of prehydrolyzed S-40% pulp would therefore seem to be slightly better, and the selectivity of prehydrolyzed S-20% pulp significantly better than that of the reference pulp. Interestingly, selectivity has been reported in the literature to be enhanced with increasing hemicellulose content (Zou et al. 2002; Zou 2002). One explanation for this finding has been that hemicelluloses act to protect the cellulose from radical attack of free hydroxyl radicals (OH·) (van

Heiningen and Violette 2001; Zou et al. 2002), thus hindering cellulose degradation. The peeling reactions of hemicelluloses would also consume alkali, thus decreasing the amount of alkali available to react with cellulose. The amount of cellulose and its degree of polymerization are the major contributors to the viscosity of pulp due to its high degree of polymerization (Zou et al. 2002). Unlike in the experiments of Zou et al. (2002), where initial kappa numbers were low (16.3 to 17.6) and the kappa number reductions in the O_2-stage were rather low and uniform (approximately 35% to 38%), the kappa numbers in this work and consequently also the kappa number reductions were higher. The kappa number reductions also varied more significantly, being higher with prehydrolyzed chips. Although the viscosity loss of pulp 1 (225 ml/g) was lower in the O_2-stage than that of pulps 2 and 3 (250 and 270 ml/g), the selectivities of prehydrolyzed chips were higher. In this work, it would therefore seem that the higher kappa number reductions of prehydrolyzed chips contributed more to the selectivity than the loss of viscosity.

The Effect of Prehydrolysis on Bleachability of Pulps

The term bleachability is used to describe the ease of bleaching of a given pulp, but there is no standard method to evaluate the bleachability of pulps. Usually, bleachability of pulp is the consumption of bleaching chemicals required to reach a given brightness. Results from bleaching of pulps 1, 2, and 3 are presented in Table 3. The chemical consumptions as total active chlorine (kg Cl/ton of pulp) in the DED-bleaching sequence are shown in Fig. 2.

Table 3. Bleaching Chemical Dosages in the DED-sequence and the Development of ISO-brightness and Pulp Viscosity in Bleaching

Pulp	Kappa after O_2-stage	Stage	Act. Cl, kg/tp	NaOH, kg/tp	End pH	Brightness, ISO %	Viscosity, ml/g
1	16.1	O_2		20		37.7	1055
		D_0	32.2		1.9		
		E		19.3	12.6	54.7	1037
		D_1	10		3.6	74.1	998
2	13.6	O_2		20		42.5	1070
		D_0	27.2		1.7		
		E		16.3	12.5	58.1	1018
		D_1	10		3.8	73.7	990
3	16.4	O_2		20		39.4	1010
		D_0	32.8		1.7		
		E		19.7	12.6	56.2	953
		D_1	10		3.7	71.9	935

As can be seen in Table 3, pulp 2 had higher brightness and a lower kappa number than pulp 1 after the oxygen delignification stage. Yet, prehydrolyzed pulp 2 did not reach a higher final brightness than unhydrolyzed pulp 1 after DED-bleaching, final brightnesses being 73.7% and 74.1%, respectively. However, the lower kappa number after O_2-delignification of prehydrolyzed pulp 2 enabled a lower ClO_2-charge in the D_0-stage (15.5% lower, calculated as total active chlorine). This resulted in lower total chemical consumption in the DED-bleaching sequence, with no losses in viscosity, when the target was to reach a final ISO-brightness of 74%. At the same time, pulps 1 and 2 showed no remarkable difference in bleachability calculated as (OXE/ton)/Δkappa in the DED-sequence. Cooking of prehydrolyzed chips with a lower sulfidity level of 20% resulted in a lower final brightness (71.9%) even with the highest chemical charge calculated as total active chlorine.

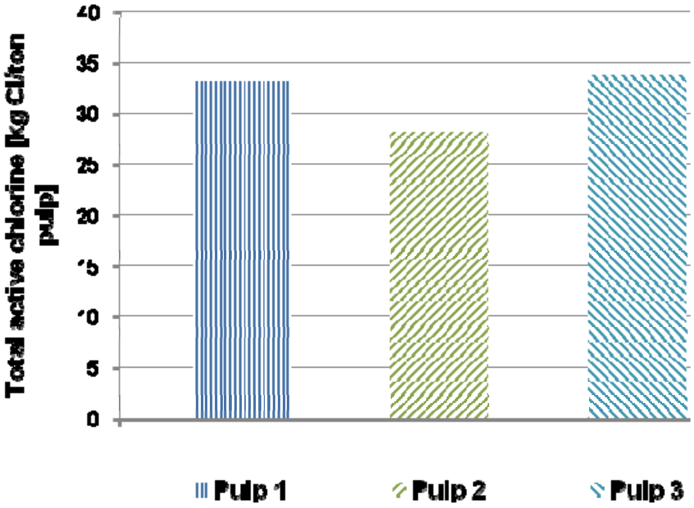

Fig. 2. Total chemical consumption in the DED-sequence calculated as total active chlorine (kg Cl/ton of pulp). Final brightnesses for pulps 1, 2, and 3 were 74.1%, 73.7%, and 71.9%, respectively.

A higher level of hydrosulfide ions in cooking, i.e. higher sulfidity, is known to have a slightly positive effect on unbleached brightness (Axelsson 2004, Gustavsson et al. 1999) and leads to better brightness development during ECF bleaching (Neto et al. 2002; Axelsson 2004). Based on our data, it can be said that the correlation between sulfidity level in cooking and pulp bleachability is markedly the same, whether or not the chips are prehydrolyzed prior to cooking. Figure 3 depicts the brightness gain throughout (O)DED-bleaching and chemical consumptions calculated as total active chlorine (kg Cl/ton of pulp) of unhydrolyzed pulp 1 and prehydrolyzed pulps 2 and 3.

As can be seen in Fig. 3, prehydrolyzed pulp 2 reached the same final brightness in (O)DED-bleaching as unhydrolyzed pulp 1 with lower chemical dosage calculated as total active chlorine (kg C/ton of pulp). Lowering the sulfidity level for prehydrolyzed pulp in cooking from 40% to 20% caused increases in chemical consumption and hindered the attainment of equally high final brightness. The same trend of increased chemical consumption and difficulties in reaching equally high brightness levels as with pulps 1 and 2 was even more pronounced with non-sulfur cooking of prehydrolyzed chips (data not shown).

Since prehydrolysis affects various aspects in the cooking process and pulp composition, some potential indirect effects of prehydrolysis on pulp bleaching will be discussed in the following paragraphs. To analyze the significance of these factors individually requires, however, further studies.

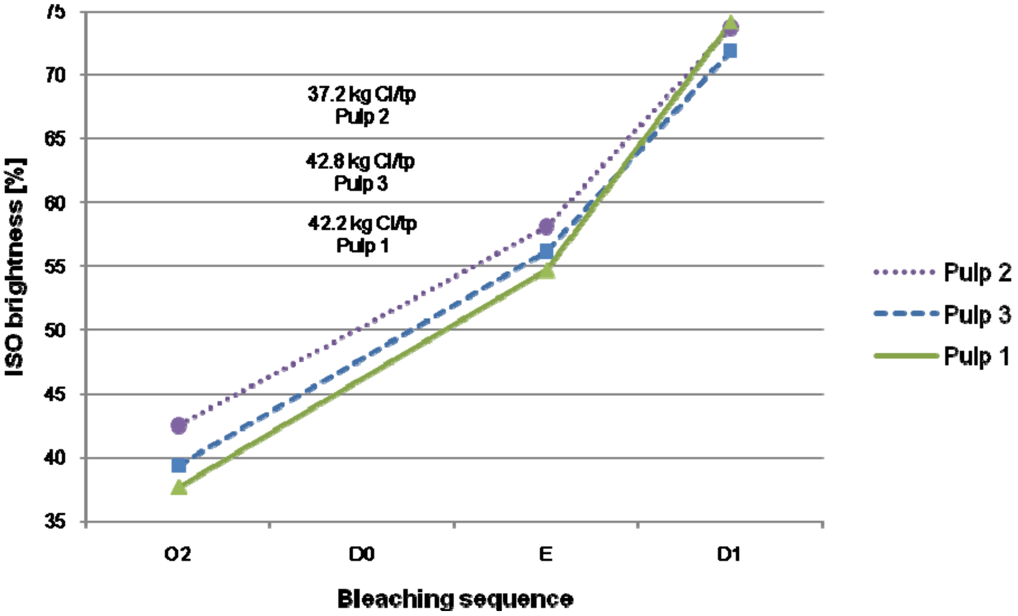

Fig. 3. ISO-brightness development in (O)DED-bleaching for prehydrolyzed pulps with chemical consumptions calculated as total active chlorine (kg Cl/ton of pulp).

Effect of cooking H-Factor on bleachability

Low H-factor is known to be beneficial for the bleaching response of pulp, at least for *Eucalyptus globulus* kraft pulps (Neto et al. 2002). A lower H-factor in cooking also results in a higher amount of alkyl-aryl ether linkages (β-O-4 structures) in residual lignin, and these kinds of pulps exhibit low specific absorption coefficients, i.e. better bleachability (Gustavsson et al. 1999). In the experiments described in this paper the prehydrolyzed pulp 2 was cooked with a lower H-factor than the unhydrolyzed pulp 1; H-factors being 1000 for prehydrolyzed and 1600 for unhydrolyzed pulp. The considerably lower H-factor of prehydrolyzed pulp 2 did not, however, lead to an increase in bleaching response compared with the reference pulp 1. One possible explanation is that the lignin fraction in water prehydrolyzed pulp has already experienced undesirable acid condensation reactions and loss of β-O-4-linkages in the prehydrolysis step, overruling the effect of a lower H-factor in cooking. Structural and chemical changes of lignin and breakage of ether linkages in water prehydrolysis have been suggested also by other authors (Antal 1996; Mosier et al. 2005; Leschinsky et al. 2007; 2008) , but the lack of effective analytical methods for evaluating lignin, both its structure and its chemical composition, hinders more complete understanding of this phenomenon (Mosier et al. 2005).

Effect of hexenuronic acids on bleachability

During kraft pulping, 4-*O*-methylglucuronic acid groups attached to xylan are partially converted to hexenuronic acid groups, forming hexenuronoxylan (Jiang et al. 2000). Hexenuronic acids (HexA) contribute to the measured kappa number in kraft pulps, 3-6 kappa number units for hardwood kraft pulp and 1-3 kappa number units for softwood kraft pulps (Gellerstedt and Li 1996). Based on previous studies (Antonsson et al. 2003; Liu et al. 2009), it is likely that the generation of hexenuronic acids during cooking is lower with prehydrolyzed pulp, since a proportion of softwood xylan is removed from the wood chips in the prehydrolysis step. Consequently, the amount of 4-O-methylglucuronic acid (MeGlcA) sidegroups attached to xylan are diminished in the pulp by respective ratio, thus lowering the amount of MeGlcA sidegroups converted to HexA during cooking of prehydrolyzed chips.

Hexenuronic acids are known to play an important role in consuming electrophilic bleaching agents such as ozone and chlorine dioxide (Vuorinen et al. 1996) and have been found to be as reactive as lignin towards these electrophilic bleaching chemicals (Vuorinen et al. 1997). In addition to increased consumption of bleaching chemicals, hexenuronic acid groups cause greater brightness reversion and poorer metal removal (Jiang et al. 2000). Therefore, when comparing water prehydrolyzed and unhydrolyzed softwood pulp, the difference in the HexA amount of unbleached pulp might also have an effect on chemical consumption in bleaching. The hexenuronic acid content of the unbleached pulps was not determined in this work, and the significance of this assumption to bleaching results should thus be verified with further studies.

Effect of metal content of pulp

Dahl et al. (1998) have studied the role of transition metal content in the D stages of pulp bleaching. According to these authors, manganese and especially iron in the process water cause loss of brightness; iron also has a detrimental effect on pulp viscosity. Lachenal et al. (1998) reported that iron in chlorine dioxide bleaching may generate Cl· radicals and therefore cause depolymerisation of carbohydrates, reducing the viscosity of pulp.

According to Sjöström (1993), transition metals in wood and pulp suspensions are partially bound to the carboxyl groups present in xylan and pectins held by the forces complexing the wood constituents, or existing as free ions in the water. Transition metals can easily be displaced and washed out of a pulp suspension (Dahl 1999). Heavy metals such as Fe and Mn can be assumed to be partially washed away somewhat similarly from wood chips in the acidic conditions of water prehydrolysis, since such metal ions can be displaced and washed out from wood by aqueous acids (Sjöström 1993).

In our study the content of the transition metals manganese and copper was lower for prehydrolyzed than for unhydrolyzed pulp, but the amount of iron in prehydrolyzed pulps was markedly higher than for unhydrolyzed pulp (see Table 4 below). High amounts of iron may have hindered the bleachability of the prehydrolyzed pulps. Since the content of other transition metals (Mn, Cu) in prehydrolyzed pulps decreased, it can be concluded that the excess iron was probably derived from the interior wall of the prehydrolysis/cooking vessel under the acidic conditions of the water prehydrolysis. This fact needs to be taken into consideration when designing equipment used for hot-water extraction of wood chips.

Table 4. Metal Contents of Examined Pulps Before Oxygen Delignification

Sample	Fe, ppm	Mn, ppm	Cu, ppm
Pulp 1	11.0	12.1	22.3
Pulp 2	30.7	8.7	9.5
Pulp 3	75.7	7.1	17.2

The Effect of Prehydrolysis on Pulp Properties

Handsheet properties were evaluated for the bleached pulps at an ISO-brightness of 74% for pulps 1 and 2, and 72% for pulp 3. Figure 4 depicts the number of revolutions in a PFI-mill required to achieve a tensile index value of 70 Nm/g for the examined pulps. Tear index values at the corresponding tensile index for each pulp are presented above the columns.

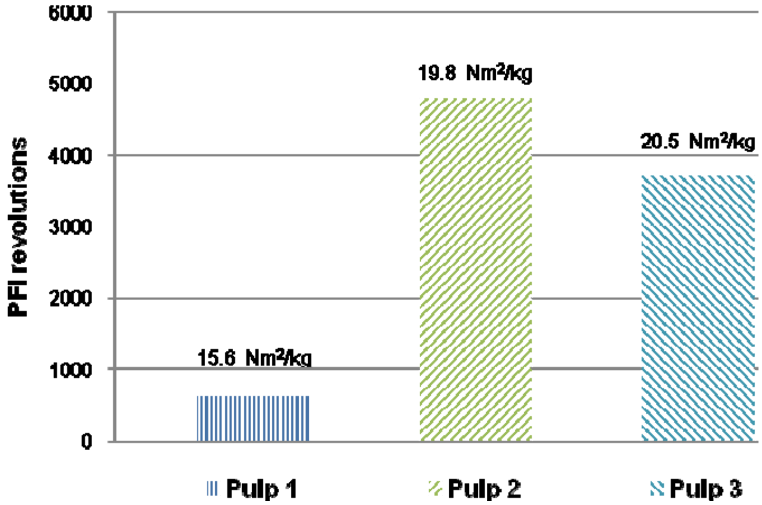

Fig. 4. Required number of revolutions in a PFI-mill in order to achieve a tensile index of 70 Nm/g. Tear index values at the corresponding tensile index are presented above each column. Respective densities for pulps 1, 2, and 3 after beating to a tensile index of 70 Nm/g were 705, 720, and 720 kg/m^3, respectively.

As Fig. 4 indicates, prehydrolyzed pulps 2 and 3 required considerably more beating revolutions in a PFI-mill than unhydrolyzed pulp 1 to achieve a given tensile index value. This is in line with previous findings, since shorter beating times and less energy absorption in beating is a feature of kraft pulps having high hemicellulose content (Rydholm 1967; Vaaler et al. 2002; Young 1994). Hemicelluloses contribute significantly to the swelling tendency of fibers. With increased swelling, interfiber contact during beating increases promoting faster external fibrillation and hence better beating response. As reported by Yoon and van Heiningen (2008) regarding slower beating responses for hot-water pre-extracted kraft pulps, the relation between hemicellulose content and beating response has also been observed with low hemicellulose content pulps. The significant reduction in beating response and strength development might present problems in commercialization of prehydrolyzed pulps.

The prehydrolyzed pulps in this study exhibited higher tear index values with the same tensile index value as unhydrolyzed pulp, as can be seen in Fig. 4. Consequently, prehydrolyzed pulps had better strength potential (tensile index x tear index) than unhydrolyzed pulp. Strength potential values were plotted as a function of sheet density (not shown), and the highest strength potential (tensile index x tear index) for both unhydrolyzed and prehydrolyzed pulps was achieved approximately at density 700 kg/m^3. Table 5 presents values of pulp properties interpolated to the density value 700 kg/m^3.

Table 5. Properties of pulps 1, 2, and 3 at Density 700 kg/m^3. Values are Interpolated to the Given Density

Property	**Density [kg/m^3]**	**Pulp 1**	**Pulp 2**	**Pulp 3**
Cellulose/hemicellulose ratio		4.9	10.6	10.1
Beating revolutions [-]	700	525	2395	1585
CSF [ml]	700	684	668	677
Tensile index [Nm/g]	700	67.1	58.2	62.1
Tear index [Nm^2/kg]	700	16.2	22.6	23.9
Tensile stiffness index [kNm/g]	700	6.87	6.17	6.60
Gurley air permeance [µm/Pas]	700	37.6	42.5	42.1
Light-scattering coefficient [m^2/kg]	700	22.7	23.8	24.2
Opacity [-]	700	69.2	72.0	74.8

Table 5 shows that as approximately half of the hemicelluloses were removed by water prehydrolysis, pulps 2 and 3 required considerably more beating revolutions in a PFI-mill than pulp 1 in order to reach the density level at which the highest value for strength potential was attained. Additional beating of pulps 2 and 3 led to lower pulp freeness (CSF), yet the tensile index of these pulps was lower than for pulp 1.

A decrease in tensile index and an increase in tear index are considered to be the main features of low hemicelluloses content pulps (Kettunen et al. 1982; Molin and Teder 2002; Rydholm 1967; Spiegelberg 1966). As can be seen in Table 5, these features were also observed in this study. Tensile stiffness index was also affected. Partial removal of hemicelluloses by prehydrolysis lowers the tensile stiffness index value. The tensile stiffness index is defined as the maximum angular coefficient in the stress-strain curve of the paper. The major factor affecting this angular coefficient is the amount of fiber-to-fiber bonding (Giertz and Rodland 1979); the stronger the fiber-to-fiber bonding, the higher the maximum angular coefficient. This leads to an assumption that fiber-to-fiber bonding in the fiber network is diminished in sheets made from prehydrolyzed pulp. Reduced fiber-to-fiber bonding has been reported to decrease tensile index values (Rydholm 1967) and increase tear index values (Bronkhorst and Bennett 2002). The decreased tensile index and increased tear index of this study would therefore also support the assumption that prehydrolysis reduces fiber-to-fiber bonding in the fiber network. Also Yoon and van Heiningen (2008) have suggested that the negative effects of hot-water pre-extraction on tensile strength of kraft pulps could be explained by the low interfiber bonding ability of the hemicellulose-poor pulps.

Prehydrolyzed pulps 2 and 3 formed sheets with a higher light-scattering coefficient (LSC), opacity and air permeability than unhydrolyzed pulp 1. The optical properties, LSC and opacity, were even better when prehydrolyzed pulp was cooked at a lower sulfidity level, 20% instead of 40%. Compact, narrow, and thick-walled fibers are known to form a porous paper that has high ability to scatter light.

Therefore, the dimensions of prehydrolyzed softwood fibers had likely changed compared to unhydrolyzed fibers, enabling more opaque, porous, and light-scattering sheets. Similar properties for paper sheets with various hemicellulose contents have also been reported by Hunger (1983) and Santos et al. (2008). Increased LSC and opacity also indicate decreased interfiber bonding in sheets made from prehydrolyzed pulps, since increasing interfiber bonding with fibrillar fines is known to have a negative effect on LSC (Luukko and Paulapuro 1999), and opacity is increased by decreasing interfiber bonding with debonding agents (Talaeipoor and Imani 2008). Therefore, differences in interfiber bonding are likely to be the main cause for the differences in the paper properties between prehydrolyzed and unhydrolyzed pulps.

CONCLUSIONS

1. The cooking of prehydrolyzed chips is significantly faster than that of unhydrolyzed chips. To obtain similar kappa numbers at similar cooking temperatures, the prehydrolyzed chips require approximately 40% shorter cooking times.
2. Prehydrolysis at P-200 decreases the pulp yield on wood by approximately 7.2 percentage units.
3. The response to oxygen delignification is higher with prehydrolyzed chips, allowing cooking to be stopped at higher kappa numbers.
4. The same final brightness (74% ISO) in (O)DED-bleaching can be reached with lower chemical consumption when wood chips are prehydrolyzed prior to cooking and cooked with a similar sulfidity level.
5. Prehydrolyzed pulps require considerably more beating to reach a specific pulp freeness (CSF) or tensile index than unhydrolyzed pulp, but exhibit higher strength potential (tensile index x tear index) at given densities.

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