Mild steam explosion: A way to activate wood for enzymatic treatment, chemical pulping and biorefinery processes

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SUMMARY: Industrially chipped wood chips of Norway spruce (*Picea abies*) were subjected to mild steam explosion (115 – 160°C) in a small-scale steam explosion reactor. This was followed by kraft cooking or extraction in alkali at 130°C for two hours, or by an enzymatic treatment with a culture filtrate in order to investigate the efficiency of the process in opening wood structure.

The results demonstrated that mild explosion has an effect on opening wood structure, shown by increased release of glucomannans during alkaline extraction and faster delignification in kraft cooks for steam-exploded samples. The effect was also shown by analysis of the released reducing sugars of enzymatic treated wood chips, which showed that the wood structure became accessible for enzymes even at very modest mild steam explosion conditions. This was not observed in untreated wood chips, used as reference. The enzyme activity increased with increased temperature during mild steam explosion, and the effect did not seem to be linear. The mechanical effect of steam explosion seems to be of great importance at lower temperatures, and both chemical and mechanical effects are important at higher steam explosion temperatures. Samples for enzymatic treatment were taken both from the edges of wood chips as well as from the middle part of the chips, and the effect of steam explosion was somewhat greater in samples from the middle parts.

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Norway spruce (*Picea abies*) is by far the most common tree in Scandinavian forests and one of the most important renewable raw materials in Northern Europe. Traditionally it has been used as sawed timber for e.g. construction and furniture, and as raw material for mechanical and chemical pulping used mainly for making paper and board, and for making regenerated cellulose and cellulose derivatives. Chemical pulping is particularly interesting since it, besides the main product which consists primarily of cellulose fibers and hemicelluloses, also produces valuable by-products. Some examples of established products made in connection with the kraft and sulfite processes are tall oil; a raw material in many chemicals including soap, or raw turpentine which is used as a raw material in solvents and chemicals. Other by-products are for example sugars for fermentation to ethanol, and lignosulfonates that among other things, are used as dispersing agents in concrete. A relatively pure lignin from the kraft process is possible to obtain through the so called LignoBoost process (Öhman et al., 2007, Theliander, 2008), which is soon to be commercialized in full scale. Methods for obtaining hemicelluloses from kraft pulping, however, need to be further developed. Thus, chemical pulping can be the base for developing biorefinery concepts, where the different components of spruce are fractionated into forms suitable for different applications in a manner similar to the petroleum industry (Kamm et al., 2006, van Heiningen, 2006, Persson, 2009). Although wood-based biorefineries today, due to greater interest in sustainable products and processes, generate great interest and research resources (Ragauskas et al., 2006, Willför et al., 2008, Alonso-Sande et al., 2009), one problem is that during chemical pulping much of the hemicelluloses are degraded, in particular the (galacto)glucomannans. This is negative since it is important for a biorefinery to be able to selectively fractionate the different components in high yields. Improved energy and material efficiency would enable potential to produce high value, low volume products parallel with low value, high volume fuels and products (Kamm, Kamm, 2004, Bozell, 2010).

The potential of using enzymes in a wood separation process is attractive since enzymes are very specific and would be able to cut explicit bonds between the wood components. Different enzymes have different specificity suitable for cellulose, hemicellulose, and lignin structures and many enzymes today are commercially produced in large quantities and applied in, for instance, the textile and food industries (Kirk et al., 2002). One problem with the fractionation of different wood components is that lignin crosslinks different wood polysaccharides into large networks that work as obstacles to the extraction and separation of wood components (Jeffries, 1990, Jung, Ralph, 1990, Lawoko et al., 2006). Recently, it was demonstrated that enzymatic treatment can increase the efficiency of the extraction of hemicellulose and lignin from pretreated wood (Azhar et al., 2011), probably by breaking up lignin-carbohydrate networks through specific enzymatic cleavage. However, wood has such a compact structure that molecules the size of enzymes cannot directly penetrate the cell walls (Blanchette et al., 1997), which means that some "opening" of the wood is necessary. An alkaline pre-treatment can achieve this efficiently (Wang et al., 2011), but also here glucomannans will be lost (Wigell et al., 2007).

An efficient and industrially feasible method to separate wood components in a selective manner is needed in order to be able to use glucomannans, lignin and the other

hemicelluloses for material purposes. Mild steam explosion, investigated in this study, could be an interesting pre-treatment for use in such a separation process. Steam explosion (STEX) is a method where wood chips, or other types of biomass, are subjected to high pressure steam, followed by a rapid release to substantially lower pressure. The liquid inside the wood chips vaporizes which leads to a rupture of the wood structure (Overend, Chornet, 1987). In this way, mild steam explosion may enhance diffusion, extraction and open the structure for enzymatic treatments.

Traditionally, steam explosion has been performed at high temperatures/pressures, with the goal of separating the fibers in wood chips and, for example, for producing fiberboard (Boehm, 1944) or fermentable sugars for bioethanol production (Saddler et al. 1982, Grethlein, Converse 1991, Schell et al. 1991, Martin et al. 1995). During steam explosion, the increase in temperature also leads to the release of acetic acid from the wood, leading to a lower pH. The slightly acidic conditions lead to degradation reactions such as acidic hydrolysis which could lead to breakage of the glycosidic bond (Sjöström, 1993), and consequently, the degree of polymerization of the polysaccharides becomes lower. This phenomenon is often referred to as autohydrolysis. Further degradation products, such as furfurals and uronic acids may also be formed (Fengel, Wegener, 1989). Steam explosion therefore not only affects the structure of wood chips, but also affects the chemical composition of the wood as hemicelluloses are degraded to a great extent when the temperature is relatively high (Grethlein, Converse, 1991, Shimizu et al., 1998). By using milder conditions (lower temperature/pressure) and a stabilizing chemical pretreatment, it might be possible to make the wood structure more open and accessible, and at the same time retain larger amounts of the hemicelluloses in the wood.

During both alkaline and acidic conditions, hemicelluloses and especially (galacto)glucomannans, are degraded to a great extent due to, for example, hydrolysis and peeling reactions. Stabilization of the hemicelluloses is therefore necessary if a high yield is to be obtained at a high pH, and one possibility is to use a reducing agent, such as $NaBH_4$, in order to increase yield and retain high molecular weights of glucomannans (Meller, 1953, Hartler, 1959). The conversion of the reducing end-group from an aldehyde to an alcohol protects the gluco-mannans from, for example, so called peeling reactions which usually occur in alkaline conditions.

If the process of mild steam explosion and extraction of some hemicelluloses is to be integrated before an ordinary kraft pulping process, it is also important that the cellulose fibers are not damaged or degraded and that the pulp has properties equal to or better than ordinary kraft pulp.

In the present study, the focus was on investigating the potential of using steam explosion at very mild conditions in order to open the wood structure slightly, with as small changes to the chemical composition of the wood as possible, and at the same time making it possible for enzymes to access the components inside the wood. This makes it easier to impregnate the wood with chemicals and increase reaction rates. The opening efficiency was examined by enzymatic treatment followed by analysis of reducing sugar with dinitrosalicylic acid (DNS) (Miller, 1959), as well as with alkaline extraction and kraft cooking of mild steam-exploded wood chips. Measurements of some pulp properties after mild steam explosion followed by kraft cooking was also investigated, in order to investigate how mild steam explosion may affect the cellulose fibers.

Materials and Methods

Materials

The raw material used in this paper was industrially cut, dried wood chips from Norway spruce (*Picea abies*) obtained from a Scandinavian pulp mill. A manual selection of the wood chips was performed in order to avoid oversized or undersized chips, knobs and bark (no chips were smaller than one centimeter in length or width, and no chips were more than four centimeters in length or width, or were thicker than one centimeter).

The enzyme used was Novozym 342 (Novozymes, Denmark), a cellulolytic culture filtrate, which is a mixture of cellulases and hemicellulases containing mainly endoglucanase, exoglucanase, and β-glucosidase (Liu et al., 2009).

The cooking chemicals were NaOH (Scharlau, reagent grade), Na_2S ($Na_2S{\cdot}9H_2O$, Fischer Scientific, analytic grade) and Na_2CO_3 (Merck, analytic grade).

The DNS reagent solution contained 1% dinitrosalicylic acid (SIGMA chemical company), 1% NaOH (Fischer Scientific), 10% NaKtartate (Merck), 0.05% Na_2SO_3 (Fischer Scientific), 0.2% phenol (Merck) dissolved in water, all of analytic grade.

Pre-treatments

Mild steam explosion

Mild steam explosion experiments were performed in a small scale reactor. Fifty grams of o. d. wood chips were fully impregnated with de-ionized water, at a liquor-to-wood ratio of 10:1, overnight prior to the experiments. Vacuum was applied for 5 min followed by pressurizing to 5 bars with nitrogen gas to improve impregnation. The chips were drained and then put in the reactor, which consisted of an autoclave with a volume of approximately 1.2 liters. The lid of the autoclave had an inlet for steam and a temperature measurement device, and the pressure was released by opening the vent to the outlet in the middle of the lid. The experiments were performed batch-wise, and the biomass was exploded inside the reactor. In order to better maintain the temperature inside the autoclave, it was put in an insulated outer beaker. The chips were then heated with steam until a desired temperature was reached; this temperature was maintained for 10 min to make sure that this temperature was also obtained inside the chips. The time was estimated, using Fourier's law of heat conduction. The pressure was then released and the temperature immediately dropped and the pressure returned at once to atmospheric pressure. The chips that were later tested with enzymes were treated at different temperatures (115°C, 130°C, 145°C and 160°C) for 10 min. This was done in order to investigate if there is a threshold at

which enzymes are able to access the wood structure after mild steam explosion. For the kraft cooking experiments, the steam explosion temperature was 160°C, and for the alkali extraction experiments the temperatures were 140°C or 160°C. The temperature was maintained for 10 min before pressure release in all cases.

$NaBH_4$ treatment

Experiments were also performed on wood chips pre-treated with sodium borohydride. This pre-treatment was performed in order to stabilize the glucomannan against degradation by for example peeling reactions that occur during alkaline conditions. The wood chips were put in a water solution containing 7 w/w% (on wood) $NaBH_4$ for four days. It was then evacuated for 15 min repeatedly in order to remove the hydrogen gas that is continuously released during the reaction, as well as to fully impregnate the wood chips during the treatment.

After-treatments

Extraction in alkali

Mild steam-exploded wood chips were subjected to alkaline extraction, where the liquor had a concentration of 0.75 M NaOH, at a liquor-to-wood ratio of 10:1. The extractions were performed in steel autoclaves and the chips were subjected to a temperature of 130°C in a pre-heated polyethylene glycol bath, for two hours. The wood chips were then washed with ten liters of de-ionized water and, in order to remove the extraction liquor, were leached in de-ionized water for one week, during which time the leaching water was replaced several times. Finally, the wood chips were dried in an oven at 105°C and milled in a cutting mill, and analyzed for Klason lignin, acid soluble lignin and carbohydrate content.

Kraft cooking

The wood chips were fully impregnated with de-ionized water prior to the kraft cooking experiments. In the subsequent cooking, 100 g of wood chips (in each batch) were placed in stainless steel autoclaves. The cooking chemicals, added as NaOH, Na_2S and Na_2CO_3, were charged at a liquor-to-wood ratio of 4.5:1 (kg/kg). The effective alkali (EA) charge was 22%, the sulfidity was 35% and the concentration of carbonate in the white liquor was 0.1 M. The autoclaves were put in a pre-heated polyethylene glycol bath at 80°C for 20 min, the temperature was then increased to 170°C at 0.8°C/min and was maintained for 40, 60, 80 and 100 min. The autoclaves were cooled and the cooked chips were separated from the black liquor which was re-filtered once, and the filter cake was then displacement washed with twenty liters of de-ionized water. This was followed by disintegration in a laboratory defibrator (L&W Noram) at 3000 rpm and the filtrate was re-filtered once, and the pulp was then subjected to a second wash with fifteen liters of de-ionized water.

Enzymatic treatment

The enzymatic treatment was done on 20 mg o. d. wood samples. Experiments were performed on samples cut into small pieces from different parts of the wood chips (dimensions approximately of a cube with a side length of a few millimeters), and on samples disintegrated by a disintegrator designed according to ISO 5263-1:2004. After cutting or disintegrating, the samples were put in eppendorf tubes together with 20 mM pH 7 phosphate buffer and 20 µl enzyme with an original activity of 90 ECU/ml. The reaction was performed in a Thermo mixer comfort (from Eppendorf AB Stockholm Sweden) at 40°C and 600 rpm shaking for 24 h. All reactions were done in duplicate and then terminated by increasing the temperature to 99°C.

Chemical analyses

Klason lignin

Klason lignin is defined as the residual material after hydrolysis of the samples through treatment with 72% sulfuric acid. The method used is based on the procedure presented by Theander and Westerlund (1986).

Two hundred mg of (o. d.) sample was weighted and 3 ml of 72% H_2SO_4 was added for each sample. The samples were then evacuated for 15 min and put in a 30°C water bath for one hour. 84 g of distilled water was added to the samples and they were put in an autoclave at 125°C for one hour. Next, the solid residue was filtered off and the filtrates were diluted up to 100 mL in round flasks. A ten times weaker solution was prepared by diluting the concentrated sample and this was used for UV measurement in order to calculate the content of acid soluble lignin, as well as for the following HPLC-measurements. For the HPLC-measurements, the hydrolysate was also diluted fifty times and fucose (internal standard) was added to a concentration of 8 mg/l.

Acid soluble lignin

The content of acid soluble lignin was calculated in relation to the absorbance value measured with UV at a wavelength of 205 nm on Specord 205, Analytik Jena. The content was calculated assuming an absorptivity constant of 110 $dm^3g^{-1}cm^{-1}$ (Lin, Dence, 1992).

Carbohydrate analysis

Analysis of monomeric sugars was performed on Dionex ICS-5000 HPLC system, equipped with CarboPac PA1 columns and run with NaOH, NaOH/NaAc (0.2 M) as eluents. Detection was done with an Electrochemical Detector. The software used was Chromeleon 7, Chromatography Data System, version 7.1.0.898.

The amounts of cellulose, galactoglucomannan and xylan were calculated from the carbohydrate analysis by using the assumptions and corrections described in the *Appendix*. The standard deviations of the analyses were estimated to be 0.05% for Klason lignin, 0.11% for cellulose, 0.05% for xylan and 0.14% for glucomannan based on three different measurements of untreated wood meal.

Released reducing sugar analysis

The opening efficiency of mild steam explosion was investigated by measuring the amount of reducing sugar produced during the enzymatic treatment described above; the more open the wood is, the more reducing sugars will be released. Reducing sugar is measured with the dinitrosalicylic acid (DNS) method described by Miller (1959). It is the most common way to measure polysaccharide activity, and the color reaction of the DNS reagent on reducing sugar can be used for

determining the concentration with the help of a glucose standard. After the enzymatic reaction 1 ml samples were mixed with 1 ml DNS reagent solution. The mixture was centrifuged for three minutes at the highest speed of a table centrifuge machine, 14,500 rpm, and then 1 ml supernatant was transferred to a new eppendorf tube and boiled for 5 min together with a glucose standard with known concentrations from 0.5 mM up to 4 mM, and reference sample which contained only water and DNS reagent. After 5 min the samples were cooled with ice water and the absorbance values were measured with a UV-2550 UV/VIS spectrophotometer (Shimadzu, Japan) at 575 nm. Finally, the released reducing sugar contents were calculated using a glucose standard and compared with the original samples by weight percentage.

Pulp properties

The kappa numbers and ISO brightness were analyzed according to SCAN methods; SCAN-C 1:77 and SCAN-C 11:75. Fiber lengths and fines were analyzed according to the Tappi standard on a Kajaani FS300.

Results

Sugar analysis after mild steam explosion

The results for the Klason lignin content and carbohydrate analysis of the wood chips exploded at different temperatures are presented in *Table 1*. The yields were high, indicating that not much of the material in the wood chips was dissolved under the experimental conditions used. The amounts of the glucomannans remained relatively constant and the decrease of xylans was very modest, and it is therefore reasonable to assume that the composition of the steam-exploded materials is virtually the same as for untreated wood.

In previous studies, steam explosion has mainly been used as a pre-treatment, often in combination with addition of SO_2, in order to obtain fermentable sugars. The conditions during steam explosion are a lot harsher in these studies, and the pH levels subsequently lower, which leads to extensive degradation of hemicelluloses. As an example, steam explosion of Norway spruce wood at 225°C for 5 min lead to a chemical composition (% on wood fibers) of 62% glucan, 33% lignin, 3.7% (galacto)-glucomannan and 1.9% (arabino)glucuronoxylan compared to 45% glucan, 28% lignin, 19% (galacto)-glucomannan and 7% (arabino)glucuronoxylan in the reference sample (Li et al., 2009). Similar results were found in a study on spruce sawdust, which was impregnated with H_2SO_4 and subjected to steam explosion at 180°C for 10 min (Söderström et al., 2003).

The effect of autohydrolysis during mild steam explosion was also investigated in an earlier study (Saltberg et al., 2011). A steam-exploded batch of wood chips was prepared at 160°C and was subjected to leaching in water at room temperature for a week, in order to measure the decrease in glucomannan content. The findings suggested that a small part of the glucomannans was degraded due to autohydrolysis during steam explosion at this temperature; the remaining glucomannan content was approximately 15% of wood. There were only very small changes in cellulose and lignin content.

Extraction in alkali after mild steam explosion

The alkali extraction experiments were done using two batches of wood chips; one was water-impregnated and the other was pre-treated with $NaBH_4$ and both samples were extracted at 130°C for two hours. Results for glucomannan content from sugar analysis of the solid residues after the extraction are shown in *Fig 1* for both batches. There is a large difference in the remaining glucomannan content between the two batches and one reason is due to the stabilization of the end-groups of the glucomannans during the $NaBH_4$ pre-treatment, which protects the glucomannans from peeling reactions under alkaline conditions.

Table 1. The results from carbohydrate analysis of non-exploded and steam-exploded wood chips. The results are presented as percentages of sample, and the non-exploded values are averages from three independent samples.

Sample STEX temp.	Yield (%)	Klason lignin (%)	Cellulose (%)	Glucomannans (%)	Xylans (%)	Non-detected (%)
Non-exploded	100	27.4	40.8	16.6	5.6	8.9
115°C	100	27.9	39.1	16.9	5.9	9.7
130°C	99.4	28.4	40.7	18.0	5.7	6.6
145°C	99.1	27.0	40.8	17.0	5.1	9.5
160°C	99.2	27.4	41.2	17.6	5.0	8.1

Table 2. Results from measurements of pulp properties. Reference cooks with different times at cooking temperature compared to kraft cooks (at the same conditions) for wood chips pretreated with steam explosion (STEX) at 160°C, 10 min.

Sample R= Ref., S= STEX	Final yield (%)	Kappa number	Viscosity (dm^3/kg)	Fiber length (mm)	ISO-Brightness
R, 40 min	49	35.6	1100	2.58	35.9
R, 60 min	48	26.3	1045	2.54	37.6
R, 80 min	47	21.0	924	2.48	38.0
R, 100 min	44	16.6	876	2.54	38.7
S, 40 min	46	33.3	1169	2.62	36.2
S, 60 min	46	21.4	1016	2.49	38.8
S, 80 min	44	18.3	948	2.57	39.9
S, 100 min	42	15.9	854	2.43	39.5

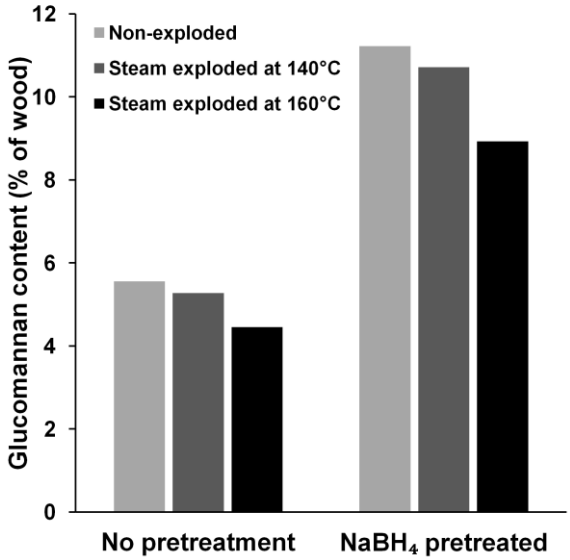

Fig 1. The figure shows a comparison of the effect of mild steam explosion for the two batches treated at different temperatures. All the samples were treated with alkali after steam explosion. Glucomannan is presented as a percentage of wood. Glucomannan content in native wood is between 16-18% of wood.

The steam-exploded samples had a greater release of glucomannans than the ones not subjected to steam explosion. The two most plausible reasons for this are an opening of the wood structure or an effect of autohydrolysis, or a combination of both.

Kraft cooking after mild steam explosion

A kraft cook series, comparing mild steam-exploded and water-impregnated wood chips, was performed in order to investigate if the increase in temperature and the pressure release during mild steam explosion influenced a subsequent kraft cook. It was found that, at the same cooking temperature, a slightly lower kappa number was reached at a given cooking time for the mild steam-exploded wood chips, as can be seen in *Fig 2*. Consequently, the overall delignification rate was higher in the steam-exploded chips. One plausible reason is that the mass transfer of cooking chemicals inside the wood chips occurs faster, which in turn indicates that the structure of the wood chip has been changed. Similar results were obtained in a study by Martin-Sampedro et al. (2011) on steam explosion followed by kraft cooking of wood chips from *Eucalyptus globulus*. The conditions during steam explosion were however harsher (190°C during 5 or 10 minutes), and 500 grams of wood chips were used for each batch. The steam pre-treatment reduced the cooking time from 50 to 20 min, obtaining a similar pulp. The mechanical properties were slightly lower, and the optical properties were higher than the control pulps.

Measurements of some of the pulp properties indicated that mild steam explosion did not affect the pulp negatively to any large extent, see *Table 2*. The fiber length was maintained at the investigated conditions; the average fiber length was about 2.5 mm in all batches. The amount of fines was also measured and showed no

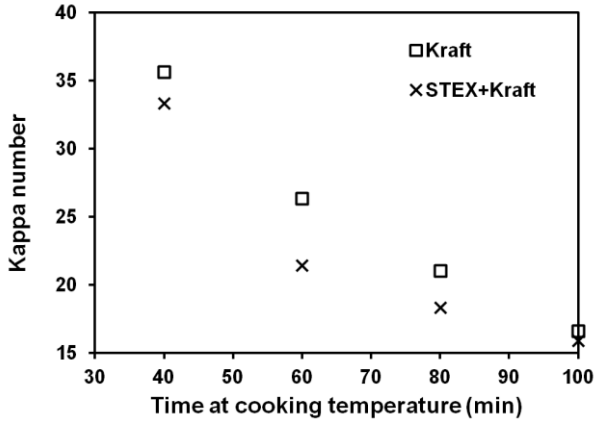

Fig 2. The pulp kappa numbers after 40, 60, 80 and 100 min at cooking temperature (170°C) for both mild steam-exploded and reference samples.

significant difference between the steam-exploded and the reference samples. The steam-exploded samples showed a slightly higher ISO brightness at the same kappa number, but the values were in the same range for both batches.

Enzymatic treatment after mild steam explosion

Samples from the mild steam-exploded wood chips were cut out into small pieces. The samples were taken from two different places; close to the edges as well as from the middle of the chips, in order to investigate if mild steam explosion has more or less effect on different parts of the wood chips. In order to get a value independent on where the samples were taken from, some wood chips were also disintegrated into small pieces before analysis. The driving force of mechanical treatment is the pressure difference between the inner part of the wood chips and the surroundings. The maximum pressure difference is between the saturation pressure and the surrounding pressure just at the moment when the pressure is released, and the results from the analysis of reducing sugar and enzyme activity in the samples are, therefore, presented versus the maximum overpressure, see *Fig 3*. According to results, some reducing sugar was released even at a very moderate temperature (115°C) during the mild steam explosion, while no reducing sugar was released in the original, non-exploded wood samples (absorbance value of 0.035, which is the same as for the zero sample with only water and DNS reagent). This indicated that the wood structure, to some extent, was opened to the enzymes even at very modest pressure differences. The results for the disintegrated samples showed a larger reducing sugar content than the local samples up to a STEX temperature of 145°C, and this is likely due to more available surfaces for the enzymes. Disintegration in itself did not result in any released reducing sugars, as can be seen in *Fig 3* where the samples which were disintegrated but not treated with enzymes resulted in nearly zero absorbance. This difference between disintegrated samples and small wood pieces could not be observed in the samples treated at 160°C.

There was generally an increase in enzymatic cleavages for samples treated at higher temperatures during steam explosion, which could be expected due to the greater

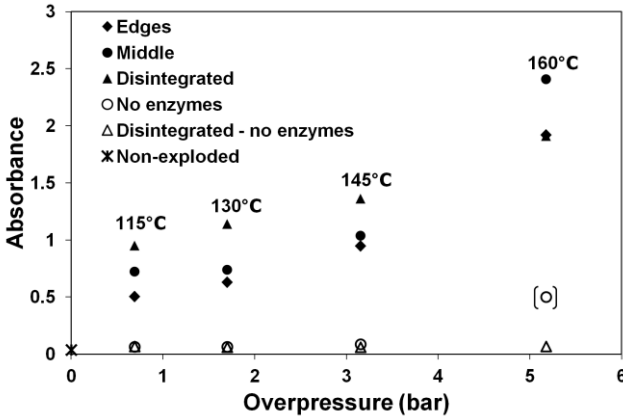

Fig 3. Results from the analysis of reducing sugar, where the absorbance at 575 nm was measured for wood chips steam-exploded at different temperatures. The steam explosion temperatures were recalculated to corresponding over pressure in the autoclave. The samples were taken from both the edges and the middle part of the wood chips, and measurements of disintegrated samples were also taken.

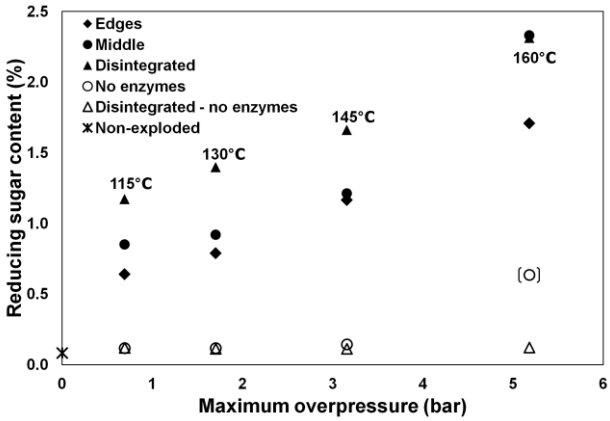

Fig 4. Results from analysis of reducing sugar recalculated to reducing sugar content. Reducing sugar content in samples taken from different parts of the wood chips and treated at different temperatures during mild steam explosion.

effect of the pressure release at higher temperatures/ pressures. Even if there are relatively few data points, it does not seem like there is a direct linear dependence of the steam explosion pressure/temperature and the measured absorbance. The increase in absorbance between 115-145°C is consistently only slightly nonlinear but it becomes clearly nonlinear when the data points at 160°C are added. It should also be remembered that chemical reaction rates generally increase exponentially with temperature (cf. Arrhenius equation). Thus, the results suggest that at the lower temperatures (115 and 130°C); the influence of mechanical forces is of great importance, and at the higher temperatures, especially at 160°C; the additional effects of chemical reactions (autohydrolysis) become more important.

Even if there is not a large difference between the samples from the edge parts of the wood chips compared to the samples from the middle parts of the chips, except for the samples treated at 160°C, the samples from the middle parts consistently results in higher absorbance values. For the samples steam-exploded at 160°C, there is a more distinct difference and a plausible explanation is that the effect of the pressure release during steam explosion is greater in the middle parts as the temperature increases.

Fig 4 shows the absorbance values recalculated into reducing sugar content by the use of a glucose calibration curve. The results from the investigation using enzymes interestingly show that mild steam explosion, also at very low temperatures, makes the structure available for molecules of the size of enzymes. Since enzymes are rather large molecules and have to be positioned in a specific way to act on a substrate, and that activity on steam-exploded wood chips was found but no activity at all on untreated wood, the findings suggest that the structure of wood is opened by steam explosion. At higher temperatures this may also be an additional effect of autohydrolysis.

Discussion

In summary, three different tests (extraction, kraft cooking and enzymatic treatment) were conducted on steam-exploded wood chips. In all three cases it was found that the rate of the operations increased if the wood chips were steam-exploded prior to the operation. In all three cases both chemical composition and physical structure may influence the overall kinetics and a change in both of these factors probably contributed to an increase in the kinetics. Since the extraction and kraft cooking investigations were made on wood chips, the substrate had such a size that mass transfer becomes significant. Thus, even if a change in chemical structure cannot be ruled out, and probably had some impact, the findings indicate that the physical structure was changed in such a way that mass transport was enhanced. This is even more plausible if the enzymatic studies are taken into consideration, because they show a big difference between untreated wood chips and steam-exploded ones at very low temperatures (115°C). At 115°C, the rate of chemical reactions (autohydrolysis) is quite low and the residence time is short (10 minutes); consequently, the influence of chemical reactions should be minor at this low temperature (Fengel, Wegener, 1989). Consider also that enzymes are large and must be configured in a specific way relative to the substrate. Thus, the main likely explanation for the enzymatic activity at low temperatures is that the physical structure of the steam-exploded wood chips has been changed. At higher temperatures, the findings suggest that there is a combination of change in physical as well as in chemical structures.

Technical significance

Mild steam explosion is a technically feasible process that can be applied on an industrial scale. It “opens” the wood structure in a way that could be beneficial both as a first step in biorefinery contexts for the separation of different wood components based on enzymatic treatments, or as a pre-treatment for traditional pulping, where the effect may give a faster delignification in the pulping process and possibly a more homogeneous pulp. The chips remain relatively intact after mild steam

explosion, which is also positive for traditional pulping. A more even chemical profile through the chip will lead to a more homogenous kraft cook, resulting in smaller differences between the outer layer of the chip and the inner part of the chip, i.e. avoiding that some outer part of the chip is over-delignified and the inner part is undelignified.

Conclusions

Mild steam explosion has an effect on opening the wood structure. It was found that steam-exploded wood chips resulted in somewhat faster extraction of glucomannans in alkali at a fixed time and temperature, and a certain kappa number was reached with a shorter cooking time in a subsequent kraft cook, than for reference samples. The pulp properties were however not affected to any great extent.

It was also found that enzymes had activity on samples treated already at very mild steam explosion conditions, while there was no activity for untreated samples. The enzyme activity increased for wood chips treated at higher temperatures during steam explosion, and this effect does not seem to be linear. This indicated that the mechanical effects are of great importance at lower temperatures, and at higher temperatures; both mechanical and chemical effects influence the results.

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Appendix

The contents of cellulose, galactoglucomannan and xylan were calculated after carbohydrate analysis by using the following assumptions/ corrections:

- The amounts of sugars analyzed were corrected for the acid hydrolysis yield.
- Anhydro sugars were calculated from sugar monomers by the withdrawal of water (multiplication by 0.88 in the case of pentosans and by 0.90 in the case of hexosans). Glucomannan was calculated as the sum of galactan, mannan and part of the glucan. The molar ratio between the mannose and the glucose in galactoglucomannan was assumed to be 3.5:1 (Meier, 1958).
- All galactan measured is included in galacto-glucomannan, acetyl groups are, however, not included.
- Xylan was calculated as the sum of xylan and arabinan. All arabinan measured is included in the xylan.
- Cellulose was calculated as the content of glucan after subtraction of the glucan connected to the galactoglucomannans.

Cellulose = Glucose – (1/3.5)·Mannose
Galactoglucomannan = Galactose+(1+(1/3.5))·Mannose
Xylan = Xylose + Arabinose

The analyses were summed up into a mass balance with the assumption that the carbohydrates were divided into cellulose, (galacto)glucomannan and xylan, which were calculated as described above.

The concentrations of arabinose, rhamnose, galactose, glucose, xylose and mannose in the hydrolysate of the different samples are presented in *Table A*.

Table A. The sugar concentrations (mg/l) in the hydrolysate from the HPLC-measurements, the non-exploded values are an average of three independent samples.

Sample STEX temp.	Rham-nose	Gal-actose	Glu-cose	Xyl-ose	Man-nose
Non-exploded	2.8	31.0	957.7	95.9	243.3
115°C	2.7	58.8	913.3	101.7	225.4
130°C	3.7	41.9	961.6	99.6	257.1
145°C	2.7	27.9	962.3	90.0	251.9
160°C	2.7	28.2	965.8	92.1	258.8