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Chemical technology/modifications

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Hardwood kraft pulp fibre oxidation using acidic hydrogen peroxide

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Abstract: Gaining insight into the oxidation of hardwood kraft fibres using hydrogen peroxide at mildly acidic conditions was the main aim of this study. The oxidized hardwood pulp had an increased number of carbonyl groups and, when formed into sheets, an enhanced durability in water was seen due to the formation of cross-links, known as hemiacetals. The carbonyl groups formed were found to be mainly ketones with the exception of the case with longer reaction times (60–90 minutes) at 85 °C, where aldehydes were detected. Through compositional analysis it was found that mainly xylan was oxidized, likely due to the higher amount of xylan close to the surface of the fibre wall. The influence of xylan on the oxidation process was investigated using cold caustic extraction (CCE) performed prior to oxidation. When the CCE pulp was oxidized, there was an increased rate of introduced carbonyl groups and degradation was more pronounced. This is likely due to the accessible surface area being increased, caused by the formation of pores when the lower molecular weight xylan was being extracted during CCE.

Keywords: bleaching; carbonyl groups; hydrogen peroxide; oxidation; wet-strength.

Introduction

Cellulose, an abundant, economically viable and renewable resource, has been thoroughly investigated as a replacement for many fossil-based materials in order to re-

duce dependence on fossil resources. One general problem with cellulosic material, however, is that it interacts with water in various ways: if cellulose materials are to withstand aqueous conditions, compounds such as wet-strength agents need to be added, or the cellulose itself requires chemical modification. One such chemical modification that has been investigated extensively is the introduction of carbonyl groups, which introduce the possibility of forming cross-links, i. e. hemiacetals, between the cellulose chains during drying. These cross-links are not hydrolysed as easily by water as hydrogen bonds, which account for the majority of inter-molecular bonds between cellulose chains. The most common form of carbonyl-rich cellulose is dialdehyde cellulose, which is obtained through the oxidation of cellulose using sodium periodate (Kim et al. 2000). Sodium periodate is, however, both harmful to the environment and expensive. Another method that may be used is TEMPO-oxidation (Saito and Isogai 2004) which, instead of a C2-C3 dialdehyde, results in a C6 aldehyde cellulose. The cost of the reagent (2,2,6,6-tetramethylpiperidine-1-oxy radical) makes this process nevertheless unviable for large-scale production, and a more environmentally friendly and economical alternative is therefore required to make carbonyl cellulose readily available.

Previous work (Martinsson et al. 2020) has shown that the oxidation of softwood pulp using hydrogen peroxide at acidic conditions led to an increase in the formation of carbonyl groups. The utilization of a common bleaching agent, such as hydrogen peroxide, to introduce carbonyl groups could potentially open up for the large-scale production of a pulp with inherent wet-strength, without the need for the further addition of wet-strength agents, in some applications.

The reaction mechanism of hydrogen peroxide at alkaline pH has been studied extensively (Gierer 1997, Zeronian and Inglesby 1995). Most of the bleaching effect at alkaline pH is attributed to the hydroperoxide anion, which forms through the decomposition of hydrogen peroxide, between pH 10 and 12 (Zeronian and Inglesby 1995, Dence and Reeve 1996). At lower pH, hydrogen peroxide may decompose through reactions with either metals, through the Fenton reaction (Gould 1985), or through reactions with or-

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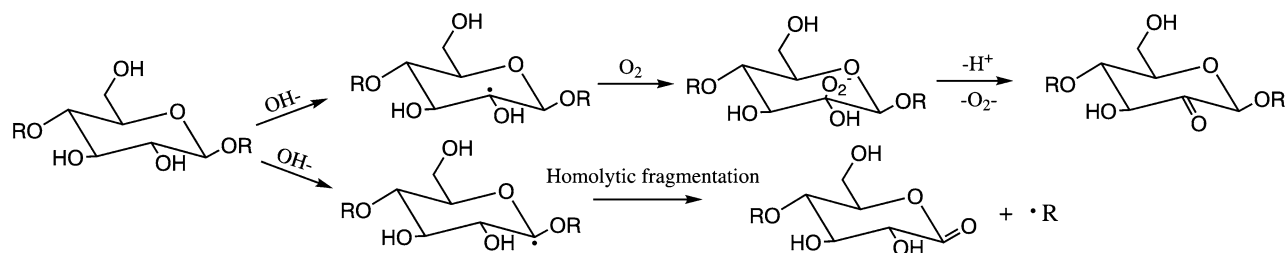


Figure 1: Oxidation of the C2 hydroxyl group into a C2 ketone (Top), and oxidation of the anomeric carbon (bottom), both initiated by hydroxyl radicals.

Table 1: Composition of pine and birch kraft pulps (Gullichsen 1999).

Component	Pine Kraft Pulp (%)	Birch Kraft Pulp (%)
Cellulose	35	34
Glucomannan	5	1
Xylan	5	16
Other Carbohydrates	–	–
Lignin	2–3	1.5–2
Extraneous Compounds	0.25	<0.5

ganic material such as cellulose (Lewin and Ettinger 1969) forming, for example, hydroxyl radicals. Hydroxyl radicals can react with the carbohydrate chains in several positions, the main ones being oxidation of the secondary hydroxyl groups or the anomeric carbon (Gierer 1997). Oxidation of the secondary hydroxyl groups is initiated by the hydrogen abstraction from the respective carbon, followed by an addition of oxygen and the subsequent formation of a ketone, Figure 1. However, according to the computational analysis by Guay et al. (2001), the third step in this reaction is energetically unfavourable at alkaline conditions. Kishimoto and Nakatsubo (1998), on the other hand, showed that during ozone bleaching, at acidic pH, the formation of carbonyl groups was mainly caused by radicals.

Hydroxyl radicals can also, in a similar fashion, oxidize the anomeric carbon (C1). The hydrogen abstraction at C1 is followed by homolytic cleavage, resulting in chain cleavage and the formation of a carbonyl group, Figure 1 (Fredricks et al. 1971, Gierer 1990).

In this study, the oxidation of hardwood kraft pulp using hydrogen peroxide was investigated and compared to previous studies of softwood kraft pulp. The introduction of oxidized functionalities, the degradation of the pulp and the influence of xylan on oxidation were investigated and are discussed in this work. Would the compositional differences, Table 1, or structural differences affect the oxidation and formation of carbonyl groups, the degradation of the pulp, or the material properties in any way? As

the high reactivity of radicals results in reactions close to the site of formation, compositional differences in the fibre surfaces may result in reactions with different structures. As the xylan content of the surface of hardwood fibres is high, whether due to the precipitation of dissolved xylan on the pulp fibres (Danielsson 2007, Hutterer et al. 2017) or to the natural distribution of xylan in the fibre wall (Sjöberg et al. 2005), oxidation is likely affect the xylan to a large extent.

Materials and methods

Materials

The original material used in the oxidation experiments was a fully-bleached hardwood (birch) kraft pulp provided by Södra Cell Mönsterås. Hydrogen peroxide, sodium acetate, sodium chloride, sodium hydroxide, bis (ethylene diamine) copper (II) hydroxide solution, sulphuric acid, sodium borohydride and sodium chlorite were of analytical quality and used as received.

Oxidation of bleached kraft pulp

Kraft pulp was oxidized in a jacketed glass reactor at a pulp consistency of 2.5% and a hydrogen peroxide concentration of 5% (mass percent of liquid fraction). The temperature was controlled using a circulating heater and the pH was kept at pH 4 using a 0.1M acetate buffer. At the end of the oxidation, 500 ml of cold deionized water was added to quench the reaction. The suspension was filtered and the filtrate was recirculated once. The filter cake was washed using 1000 ml of deionized water, after which the filter cake was transferred to a beaker containing 500 ml of deionized water; the pulp remained there for 10 minutes. The suspension was then filtered and the filtrate recirculated once, followed by a wash with 1000 ml of deionized water, adjusted with sulphuric acid to pH 3.5, to min-

imize the impact of degradation due to β -alkoxy elimination (Münster et al. 2017).

Determination of carbonyl content

The carbonyl content was determined by the use of hydroxylamine hydrochloride (Zhao and Heindel 1990), with 500 mg (O. D. weight) of never-dried pulp being used for the analysis. The pulp was added to 50 ml deionized water adjusted to pH 4 using hydrochloric acid, and left for 10 minutes. The suspension was filtered and the filtrate recirculated once, after which the sample was washed with an additional 50 ml of deionized water adjusted to pH 4. The pulp sample was then transferred to a beaker containing 25 ml of 0.25 M hydroxylamine hydrochloride (aq.) adjusted to pH 4 and left for 2 hours at room temperature and under constant mixing. It was then filtered, and the filtrate titrated back to pH 4 using 0.01 NaOH (aq.). The filter cake was washed and used to determine the exact mass of the sample. The number of carbonyl groups were calculated from the amount of NaOH (aq.) used in the titration and the oven-dry weight of the sample. All analyses were performed in duplicate.

Determination of carboxyl content

The carboxyl content was determined using a method based on the procedure of Barbosa et al. (2013) thus: 500 mg (O. D. weight) of never-dried pulp was placed in a flask containing 60 ml of 0.1 M hydrochloric acid, which was shaken to disperse the sample and subsequently left for 2 hours at room temperature in order to protonate the carboxyl groups. It was then filtered and the filtrate recirculated once, after which the sample was washed with deionized water until the filtrate was neutral. The pulp sample was then transferred to a 100 ml beaker into which 50 ml of 0.5 M NaCl (aq.) was added to control the ionic strength. The sample was then titrated using 0.02 M NaOH (aq.) in 0.5 M NaCl (aq.), after which the suspension was filtered and the pulp sample washed with deionized water and placed in an oven at 105 °C so that the mass of the sample could be determined. The carboxyl content was calculated from the volume of titrant at the equivalence point and the oven-dried mass of the sample. All analyses were performed in duplicate.

Measurements of intrinsic viscosity

The intrinsic viscosity of a sample dissolved in bis(ethylenediamine) copper (II) hydroxide solution (CED)

was determined using capillary viscosimetry according to the SCAN-C 15:99 method. Prior to these measurements being made, the samples were reduced for 24 h using a solution of sodium borohydride (3 % on pulp weight) at a consistency of 2 % to reduce the impact of degradation during dissolution. All analyses were performed in duplicate.

Compositional analysis

The carbohydrate composition of the sample was determined using a method based on the research of Theander and Westerlund (1986) and Jedvert et al. (2012). A 200 mg (O. D.) sample was put in a 150 ml beaker, into which 3 ml of 72 % of sulphuric acid was added. The beaker was first subjected to vacuum for 15 minutes before being placed in a 30 °C water bath for 1 hour, being stirred every 20 minutes. It was then diluted by the addition of 84 g of deionized water and placed in an autoclave at 125 °C for 1 hour. The sample was thereafter filtered, diluted and 8 mg/L of fucose was added as internal standard. The filter cake was placed in an oven at 105 °C for the determination of Klason lignin; the filtrate was used to determine the amount of acid soluble lignin using an Analytik Jena UV spectrometer at a wavelength of 205 nm, with an absorptivity constant of 110 dm³/g cm. The diluted filtrate was analysed for monomeric sugars using a Dionex ICS-5000 equipped with CarboPac PA1 columns, using NaOH/NaAc (aq.) and NaOH (aq.) as eluents. An electrochemical detector was used for detection and Chromeleon 7 Version 7.1.3.2425 was used as software. The sugar monomers detected were corrected for acid hydrolysis yield and converted into anhydro sugars.

Quantification of aldehyde groups

The number of aldehyde groups was quantified through the oxidation of aldehyde groups into carboxyl groups using sodium chlorite, according to the method described by Saito and Isogai (2004). A slurry with a consistency of 10 % was prepared from 2 g (oven dry weight) of pulp, and added to a mixture consisting of 1.81 g of sodium chlorite, 20 ml of 5 M acetic acid (aq.) and 57 ml of deionized water. The pH of the mixture was adjusted to 4.5 using a 50 % sodium hydroxide solution. The mixture was then placed on a shaking table for 48 h, after which the pulp was filtered off and the filtrate recirculated, before being washed with 2 L of deionized water. The carboxyl content of the samples was then analysed and the aldehyde con-

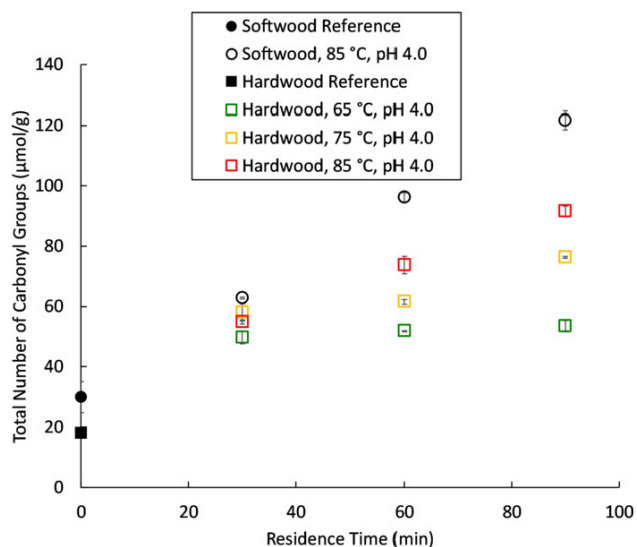


Figure 2: Total carbonyl content of hardwood pulp oxidized at temperatures between 65 °C and 85 °C, measured using the hydroxylamine hydrochloride method. Carbonyl content of softwood pulp oxidized at 85 °C included for comparison.

tent defined as the increase in the content of carboxyl after sodium chlorite oxidation.

Cold caustic extraction

Cold caustic extraction was used to remove xylan from the original material, according to the procedure of Janzon et al. (2008). A consistency of 5 % and a mass concentration of 10 % sodium hydroxide was used. The suspension was stirred continuously and kept at room temperature for 1 hour, after which it was filtered and the filtrate recirculated once. The pulp was washed using a three-stage washing sequence using 2 % sodium hydroxide (aq.), followed by 5 % acetic acid (aq.) and, finally, 2 L of hot deionized water.

Wet durability test

The durability in water of the sheets produced from oxidized and unoxidized pulp, with or without xylan, was tested by producing simple sheets that were submerged in water. 300 mg (O. D. weight) of never-dried pulp and 1 L of deionized water were placed in a standard pulp disintegrator, which was then run for 30000 revolutions. The suspension was filtered through a Büchner funnel to produce a sheet, which was allowed to air dry for three days before its durability in water was tested. A square 3×3 cm in size was cut from the sheet and placed in a beaker containing

200 ml of water and a stir bar. After a lapse of 10 minutes, any swelling that had occurred was observed; the sample was stirred for 1 minute at 120 rpm and the level of disintegration noted.

Analysis of fibre dimensions

The dimensions of the fibres were analysed using a Kajaani FS300 fibre image analyser. 50 mg (O. D. weight) of never-dried pulp was added to 2 L of deionized water and defibrillated for 30 000 revolutions in a standard pulp disintegrator. Roughly 30 ml of the suspension was then added to a beaker and analysed.

Results and discussion

Acidic oxidation of hardwood pulp

Hardwood pulp was oxidized at varying temperatures and residence times whilst a pH of 4 was kept constant. Temperatures varied between 65 and 85 °C and residence times varied between 30 and 90 minutes. The results were compared to previous results obtained from oxidations of softwood pulp (Martinsson et al. 2020). The rate of oxidation is fairly low below 85 °C, which makes comparison difficult: comparisons with softwood pulp were therefore only made at 85 °C. Oxidation resulted in an overall increase of carbonyl, as can be seen in Figure 2. Oxidation at 85 °C led to a significantly lower increase in the content of carbonyl in the case of hardwood pulp compared to softwood. The hardwood reference also showed a lower number of carbonyl groups than the softwood reference. This could be due to a number of reasons: the differing bleaching sequences, differences in fibre morphology, xylan distribution in the cell wall, etc. Comparing the intrinsic viscosity of oxidized softwood and hardwood kraft pulp, identical conditions are seen to lead to similar degradation, as shown in Figure 3, although identical conditions led to a significantly lower number of carbonyl groups being formed in the oxidized hardwood pulp. This suggests that the oxidation process is significantly slower in the case of hardwood, while the degradation reactions are similar in both cases.

The carboxyl content was quantified for the hardwood pulp samples: no trend with increasing carboxyl groups could be found, although a slight lowering of the carboxyl content with increased reaction temperature was seen, Figure 4. This is in agreement with the results obtained

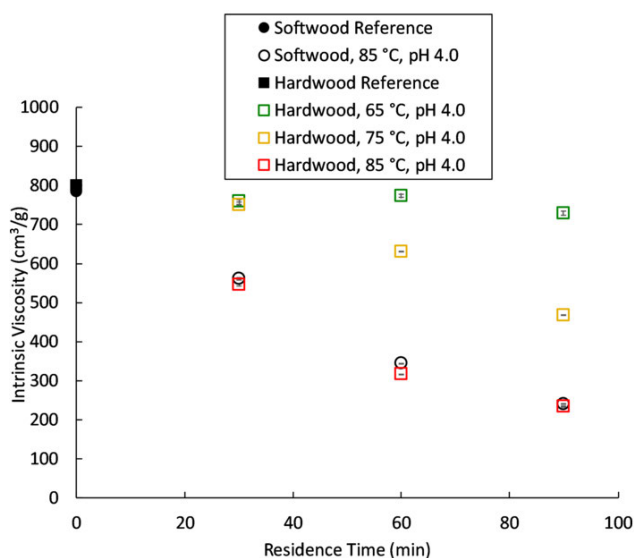


Figure 3: Intrinsic viscosity in CED for hardwood pulp oxidized at temperatures ranging from 65 °C to 85 °C, measured using capillary viscosimetry. Intrinsic viscosity of softwood pulp oxidized at 85 °C included for comparison.

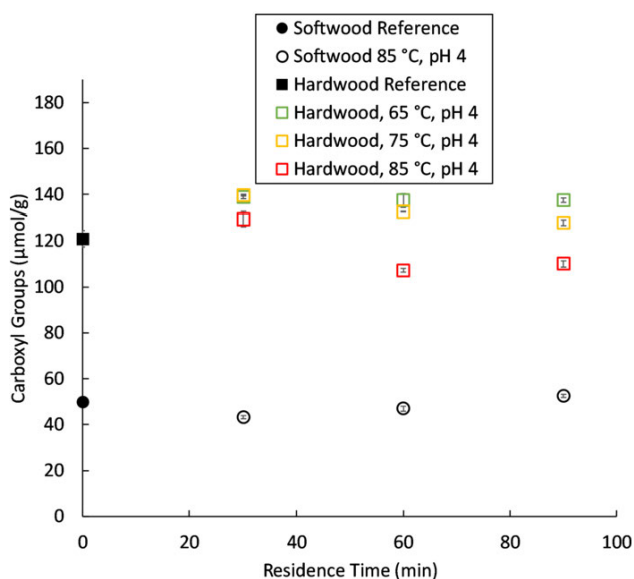


Figure 4: Carboxyl content of hardwood pulp oxidized at temperatures ranging from 65 °C to 85 °C, measured using potentiometric titration. Softwood pulp oxidized at 85 °C included for comparison.

by Lewin and Ettinger, who suggest that the carboxyl content is only affected to a minor extent when oxidizing with hydrogen peroxide (Lewin and Ettinger 1969). No significant increase in carboxyl groups was found, which suggests that the carbonyls formed are not oxidized further into carboxyl groups, indicating that mainly ketones are formed and/or that further oxidation from aldehyde to car-

Table 2: Composition of hardwood pulp samples oxidized at 85 °C.

	Reference	30 min	60 min	90 min	90 min blank run
Glu (%)	69.1	69.0	70.2	71.0	69.5
Xyl (%)	19.4	19.0	17.7	16.3	19.5
Man (%)	0.08	0.40	0.40	0.31	0.18
Klason (%)	0.32	0.20	0.10	0.15	0.12
ASL (%)	0.93	1.01	0.91	0.95	0.90
Undetected (%)	10.17	10.39	10.69	11.29	9.80

Table 3: Composition of hardwood pulp samples subjected to CCE and following oxidation at 85 °C.

	CCE Reference	30 min	60 min	90 min
Glu (%)	81.4	85.60	86.10	85.90
Xyl (%)	2.39	2.27	2.08	1.73
Man (%)	0.50	0.51	0.49	0.46
Klason (%)	0.50	0.08	0.10	0.07
ASL (%)	0.55	0.61	0.73	0.91
Undetected (%)	14.66	10.93	10.50	10.93

boxyl does not take place to any large extent. Further investigation was, therefore, necessary.

In order to evaluate the extent of the formation of either ketones or aldehydes, the samples were oxidized further using sodium chlorite to selectively oxidize any aldehydes into carboxyl groups. An increase in the content of carboxyl could then be attributed to the content of aldehydes. No increase in carboxyl content after sodium chlorite could, however, be noted except in the cases of oxidation at 60 and 90 minutes at 85 °C, respectively. A slight decrease was found for all the other cases, suggesting that oxidation at moderate temperatures (i. e. below 85 °C) targets the secondary hydroxyl groups of the carbohydrates rather than the primary C6 hydroxyl of cellulose. This could be caused by the short-lived radicals reacting with xylan on the surface of the fibres, and/or the fact that hydroxyl radicals react mainly with secondary hydroxyl groups, as reported by Lewin and Ettinger (1969) and Gierer (1997).

Evaluating the change in composition of the pulp during the course of the oxidation shows a decrease in the content of xylose, Table 2. This indicates that xylan is oxidized, since oxidized xylan would not be detected as sugar monomers after hydrolysis. The 90 min blank run, without the presence of hydrogen peroxide did not appear to change the composition to any noticeable extent, suggesting that mildly acidic conditions at the temperatures investigated do not cause any compositional changes.

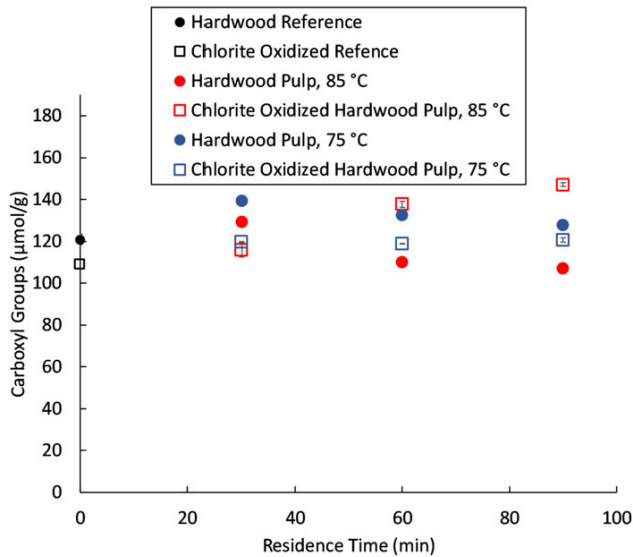


Figure 5: Carboxyl content of oxidized hardwood pulp before and after sodium chlorite oxidation.

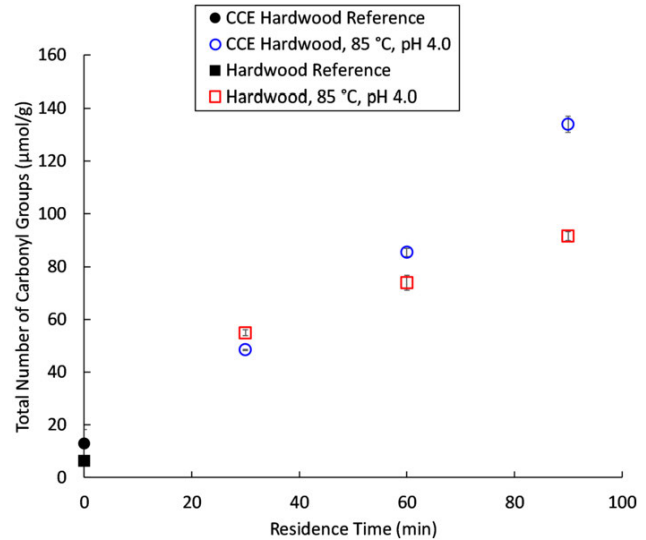


Figure 7: Total carbonyl content of CCE pulp and fully-bleached, hardwood pulp, oxidized at 85 °C.

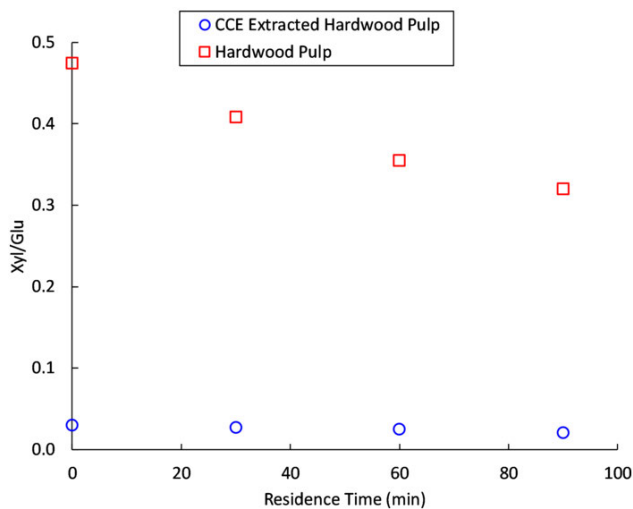


Figure 6: Relation between xylan and glucan during oxidation of hardwood pulp and CCE hardwood pulp.

Cold caustic extracted pulp

The fully-bleached hardwood pulp was subjected to cold caustic extraction (CCE) to investigate how the xylan content affects oxidation. The compositional analysis showed that around 88% of the xylan present in the sample was extracted, with further oxidation of the sample lowering the xylan content slightly more.

Comparing the relation between glucan and xylan during the oxidation of the hardwood pulp and the CCE pulp provides a way of investigating the amount of xylan that is affected by the oxidation, Figure 6. When xylan is

present in the sample, the amount decreases rapidly: in the case of the CCE pulp, on the other hand, almost all of the xylan has been removed from the sample prior to oxidation and the relation between glucan and xylan remains on a constant level throughout oxidation. A possible explanation for this is that the majority of the xylan on the surface of the fibres is extracted with the CCE, allowing for the short-lived radicals to oxidize cellulose to a larger extent than in xylan-rich fibres, rather than the residual xylan which is likely to be less accessible.

Comparing the formation of carbonyl groups in the two pulps, a larger increase in carbonyl content can be seen for the CCE pulp, Figure 7. A reason for this could be an increase in porosity due to the removal of low molecular weight compounds which, in turn, would lead to an increase in accessible surface area in the never-dried state for the CCE pulp (Dou and Tang 2017).

Comparing the intrinsic viscosity of the fully-bleached hardwood pulp with the CCE hardwood pulp, a higher intrinsic viscosity can be noted for the latter. This can be expected, as a fraction of lower molecular weight material, i. e. the xylan, has been removed during CCE. During oxidation, the CCE pulp undergoes a more rapid degradation than the fully-bleached hardwood pulp, particularly at the beginning, Figure 8. This could be caused by more extensive degradation of the cellulose once the majority of the xylan has been removed or, as reported by Borrega et al. (2018), an increased porosity and fibril aggregation, causing a decrease in the levelling-off degree of polymerisation (LODP), caused by the alkaline extraction of xylan.

It was found that oxidation of CCE pulp leads to a more rapid degradation and oxidation of the carbohydrates compared to the hardwood pulp. The increase in degradation is, however, more pronounced, as seen when the oxidation of hardwood pulp for 60 minutes is compared with that of CCE pulp for 30 minutes. Both of these oxidations result in a similar intrinsic viscosity ($317 \text{ cm}^3/\text{g}$ and $320 \text{ cm}^3/\text{g}$), while the oxidized CCE pulp has a lower number of carbonyl groups ($74 \mu\text{mol}/\text{g}$ and $48 \mu\text{mol}/\text{g}$).

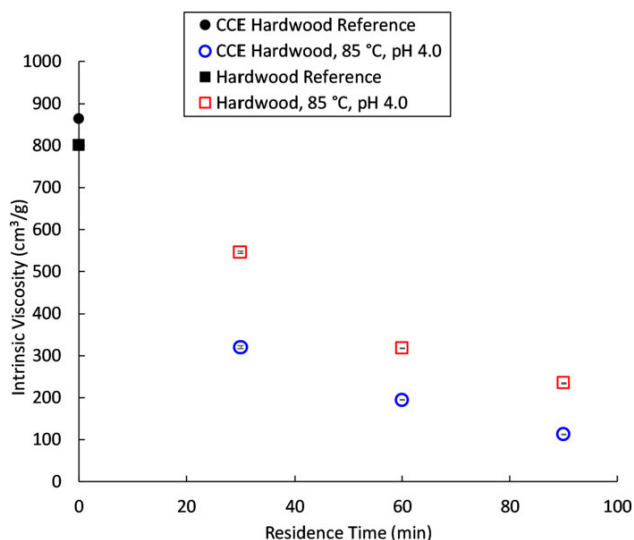


Figure 8: Intrinsic viscosity of CCE pulp and fully-bleached hardwood pulp, oxidized at 85°C .

Fibre image analysis

No significant change can be seen when comparing the results obtained from the fibre image analysis of the oxidized pulp and the fully-bleached hardwood pulp (Figure 9). CCE, on the other hand, seems to affect the fibre length distribution; subsequent oxidation of CCE pulp does not seem to affect the fibre dimensions in any way. Furthermore, when pulp from a blank run, without the presence of hydrogen peroxide, was tested it did not affect the fibre dimensions to any noticeable degree.

A comparison of the dry sheets produced from the pulps (Figure 10) showed no visual difference between the reference sheet and that produced from the pulp subjected to a blank run. The sheet made from pulp subjected to CCE was noticeably less dense and more prone to ripping, whilst that made from the oxidized hardwood pulp was clearly stiffer than any of the other samples.

The durability of each sheet in water was tested by placing it in a beaker of deionized water and, after leaving it to swell for 10 minutes, observations were made of any changes that has occurred, Figure 11. The reference and blank samples appeared to have identical degrees of swelling. The oxidized hardwood pulp maintained its dense structure, while the CCE pulp and the oxidized CCE pulp showed significant swelling.

The 10 minutes of swelling was followed by stirring at 120 rpm for 1 minute, after which the sheets were observed for disintegration, Figure 12. Complete disintegra-

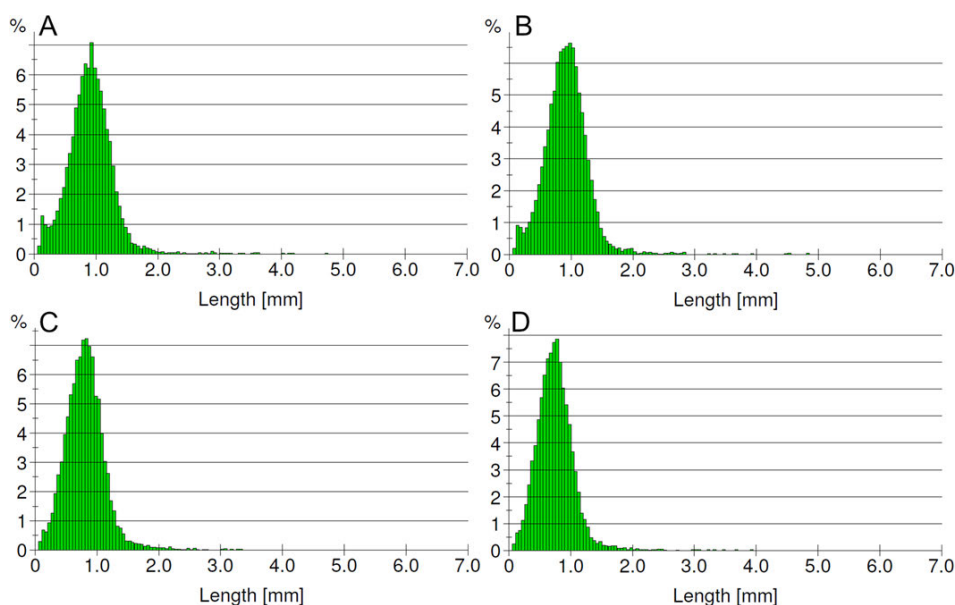


Figure 9: Fibre length distribution of the fully bleached hardwood pulp (A), pulps oxidized for 90 minutes at 85°C (B), CCE pulp (C) and CCE pulp oxidized for 60 minutes at 85°C (D).

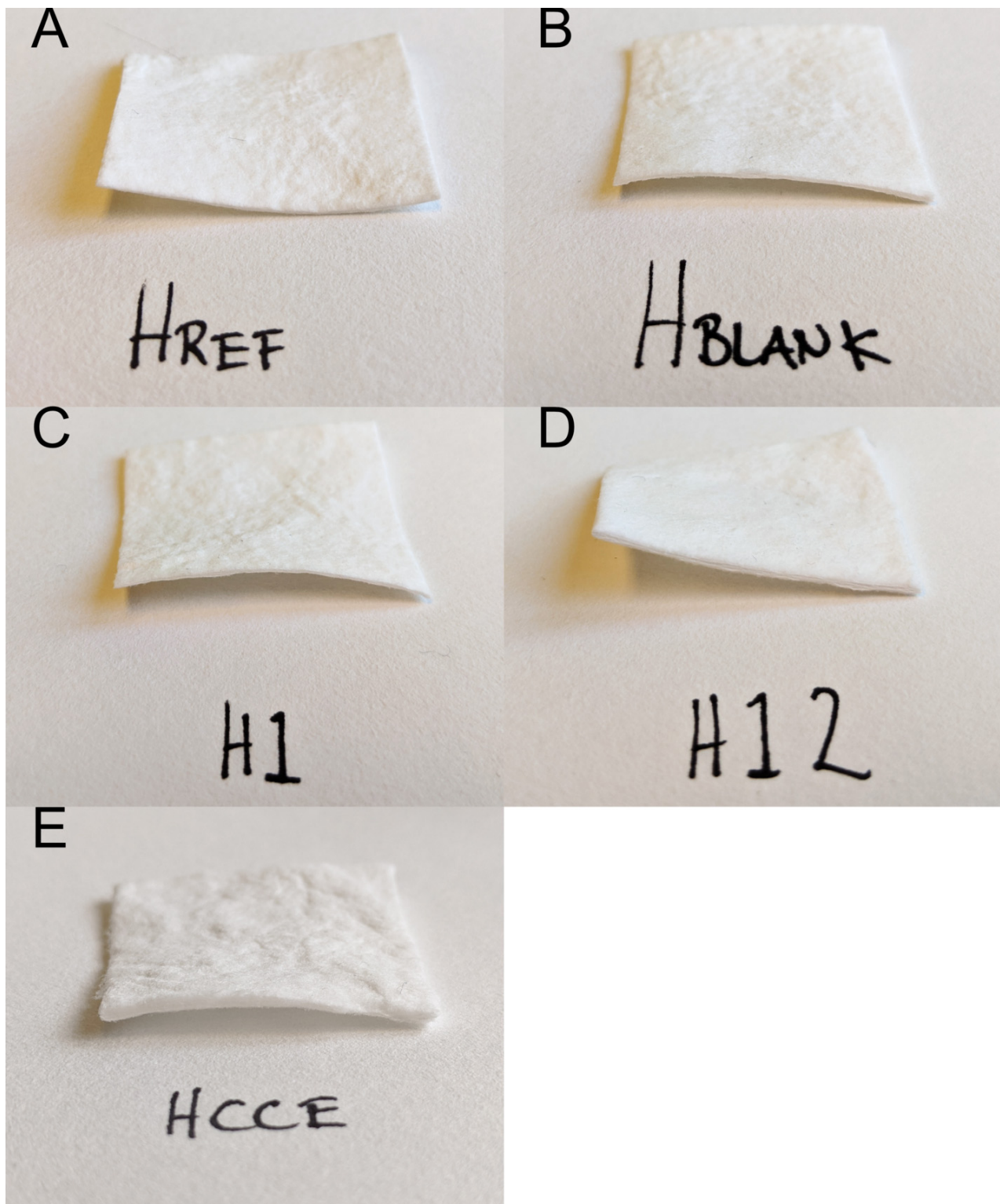


Figure 10: Pulp sheets produced from: fully-bleached hardwood pulp (A), pulp subjected to a blank run (B), pulp oxidized for 90 minutes at 85 °C (C), CCE pulp subjected to 60 minutes of oxidation at 85 °C (D) and pulp subjected to CCE (E).

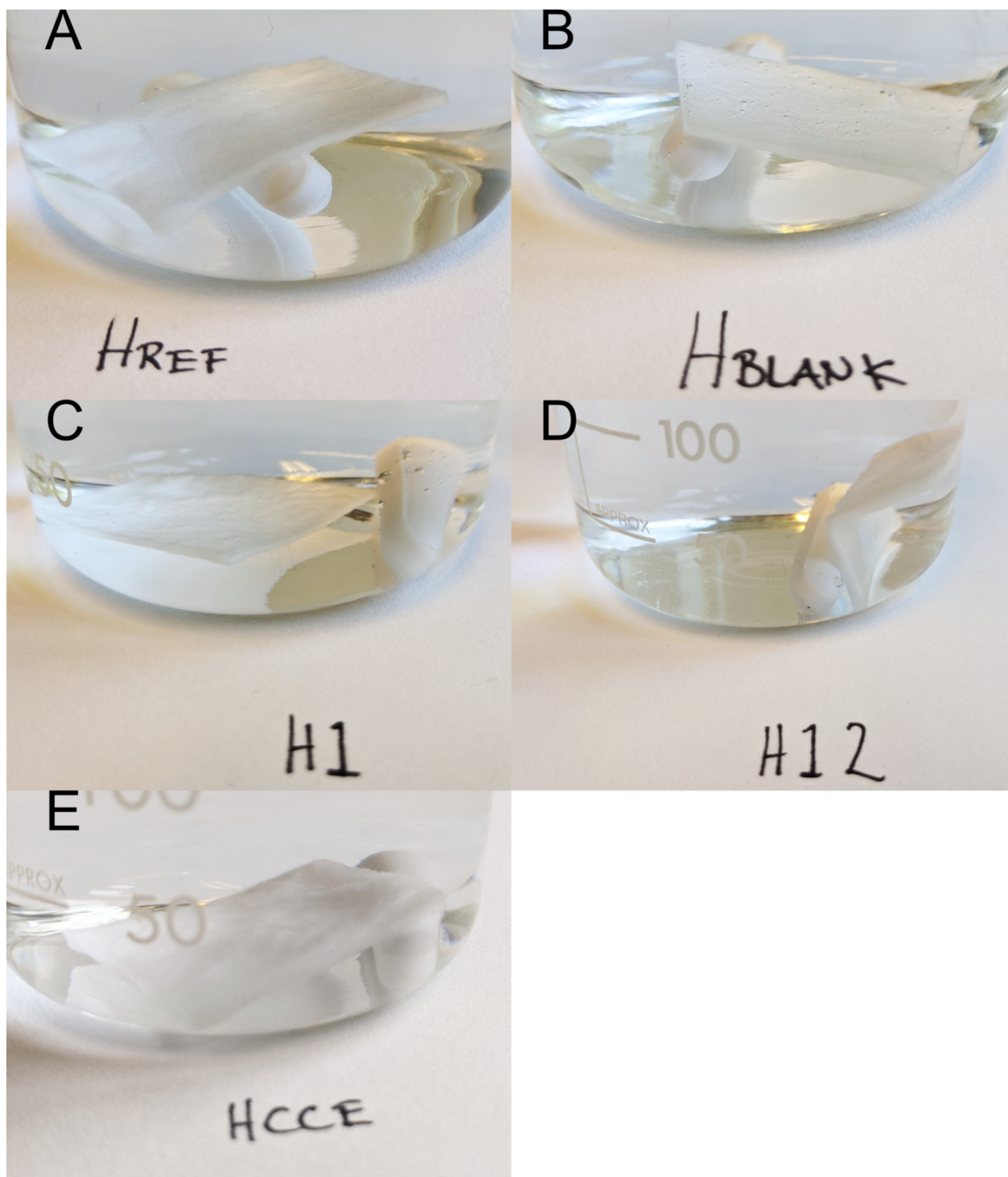


Figure 11: Pulp sheets after swelling for 10 minutes in deionized water. Fully-bleached hardwood pulp (A), pulp subjected to a blank run (B), pulp oxidized for 90 minutes at 85 °C (C), CCE pulp subjected to 60 minutes of oxidation at 85 °C (D) and pulp subjected to CCE (E).

tion could be noted for the fully-bleached hardwood pulp, the pulp subjected to the blank run and the CCE pulp. For the oxidized hardwood pulp, no disintegration could be

seen and very few loose fibres were apparent. Although the oxidized CCE pulp disintegrated partially, it nevertheless maintained some form, despite the fact that the sus-

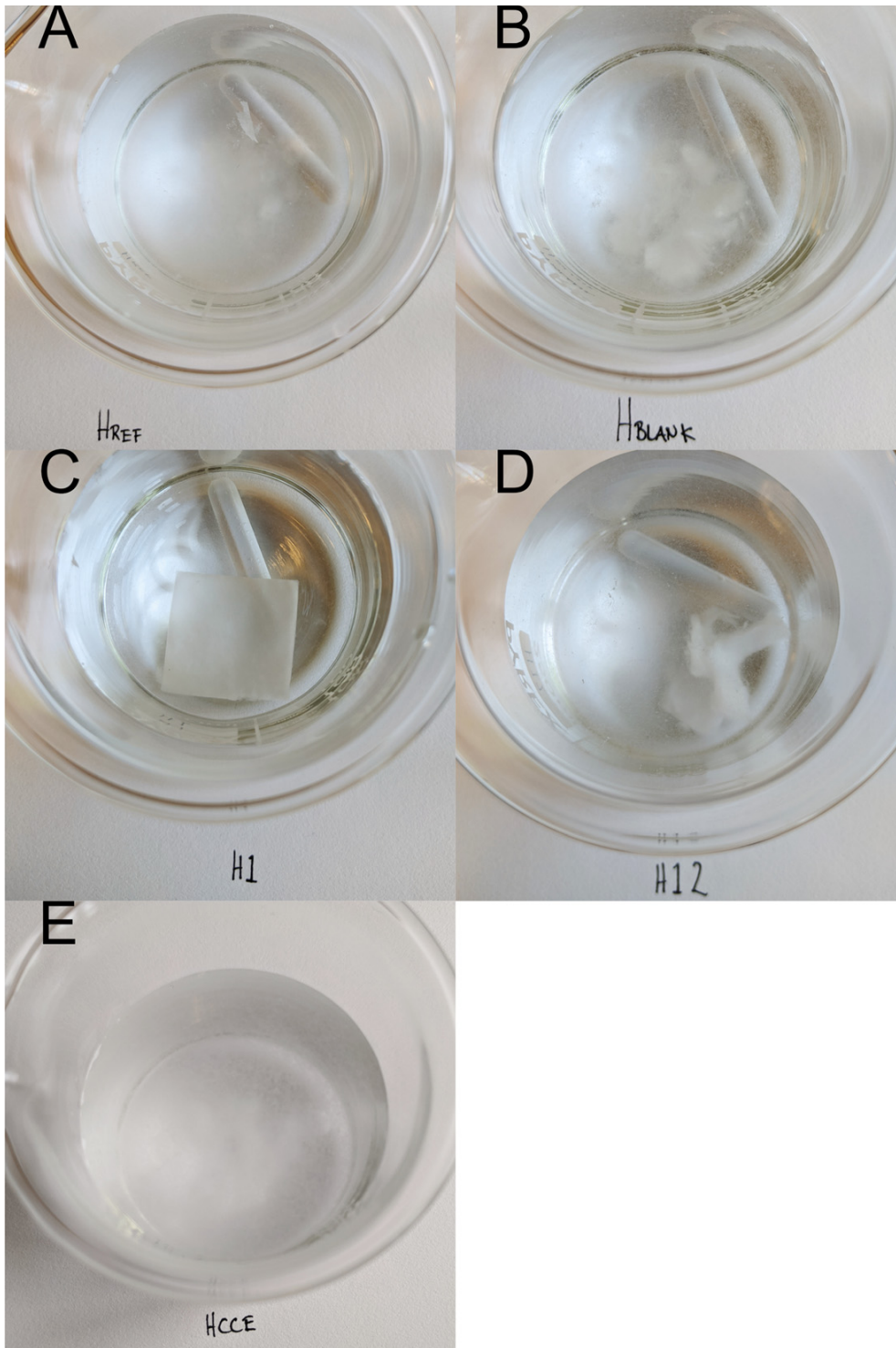


Figure 12: Pulp sheets after stirring for 1 minute at 120 rpm. Fully-bleached hardwood pulp (A), pulp subjected to a blank run (B), pulp oxidized for 90 minutes at 85 °C (C), CCE pulp subjected to 60 minutes of oxidation at 85 °C (D) and pulp subjected to CCE (E).

pension contained many loose fibres. This could be an effect of hornification, following the collapse of pores in the extracted fibres. Such increased hornification leads to fi-

bres that are less flexible, which could limit their ability to form cross-links and thereby reduce their durability in water compared to the oxidized hardwood pulp.

Conclusions

The compositional analysis of the oxidized pulp clearly shows a reduction in the amount of xylan. It suggests that hydrogen peroxide oxidation may favour the oxidation of xylan rather than cellulose, possibly due to the high availability of xylan in the cell wall.

The oxidation of secondary hydroxyl groups into ketones is favoured at temperatures below 85 °C, as shown by further oxidation with sodium chlorite, whereas the formation of aldehydes is limited at these conditions. During oxidations at 85 °C extensive aldehyde formation can be noted.

The degradation of softwood kraft pulp and hardwood kraft pulp at 85 °C are of similar magnitude, as measured by capillary viscosimetry. The formation of carbonyl groups are, however, more extensive during the oxidation of softwood pulp.

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Conflict of interest: The authors declare no conflicts of interest.

References

- Barbosa, L.C., Maltha, C.R., Demuner, A.J., Cazal, C.M., Reis, E.L., Colodette, J.L. (2013) A Rapid Method for Quantification of Carboxyl Groups in Cellulose Pulp. *BioResources* 1043–1054. 10.15376/BIORES.8.1.1043-1054.
- Borrega, M., Ahvenainen, P., Kontturi, E. (2018) Impact of hydrothermal and alkaline treatment of birch kraft pulp on the levelling-off degree of polymerization (LODP) of cellulose microfibrils. *Cellulose* 25:6811–6818. 10.1007/s10570-018-2017-7.
- Danielsson, S. Xylan Reactions in Kraft Cooking (Doctoral Thesis). Royal Institute of Technology, Stockholm, 2007.
- Dence, C.W., Reeve, D.W. Pulp Bleaching – Principle and Practice. TAPPI PRESS, Atlanta, 1996.
- Dou, X., Tang, Y. (2017) The Influence of Cold Caustic Extraction on the Purity, Accessibility and Reactivity of Dissolving-Grade Pulp. *Chemistryselect* 2(35):11462–11468. 10.1002/slct.201701551.
- Fredricks, P.S., Lindgren, B.O., Theander, O. (1971) Chlorine Oxidation of Cellulose. *Sven. Papp.tidn.* 74(19):597–603.
- Gierer, J. (1990) Basic Principles of Bleaching Part 2: Anionic Processes. *Holzforschung* 44(6):395–400. 10.1515/hfsg.1990.44.6.395.
- Gierer, J. (1997) Formation and Involvement of Superoxide ($O_2^{\bullet-}/HO_2^{\bullet}$) and Hydroxyl (OH^{\bullet}) Radicals in TCF Bleaching Processes: A Review. *Holzforschung* 51(1):34–46. 10.1515/hfsg.1997.51.1.34.
- Gould, J. (1985) Studies on the mechanism of alkaline peroxide delignification of agricultural residues. *Biotechnol. Bioeng.* 27(3):225–231. 10.1002/bit.260270303.
- Guay, D.F., Cole, B.J., Fort, R.C., Hausman, M.C. Genco, J.M., Elder, T.J., Overly, K.R. (2001). Mechanisms of Oxidative Degradation of Carbohydrates During Oxygen Delignification. II. Reaction of Photochemically Generated Hydroxyl Radicals with Mehtyl β -Cellobioside. *J. Wood Chem. Technol.* 21(1):67–79. doi:10.1081/WCT-100102655.
- Gullichsen, J. (1999) Chemical Pulping (Vol. 6). Eds. Gullichsen, J., Fogelholm, C.-J. Fapet Oy, Helsinki.
- Hutterer, C., Fackler, K., Schild, G., Ibl, V., Potthast, A. (2017) Xylan Localization on Pulp and Viscose Fiber Surfaces. *BioResources* 12(3):5632–5648. doi:10.15376/BIORES.12.3.5632-5648.
- Janzon, R., Saake, B., Puls, J. (2008) Upgrading of paper-grade pulps to dissolving pulps by netren extraction: properties of nitren extracted xylans in comparison to NaOH and KOH extracted xylans. *Cellulose* 15:161–175. 10.1007/s10570-007-9154-8.
- Jedvert, K., Wang, Y., Saltberg, A., Henriksson, G., Lindström, M.E., Theliander, H. (2012) Mild steam explosion: A way to activate wood for enzymatic treatment, chemical pulping and biorefinery processes. *Nord. Pulp Pap. Res. J.* 27(5):828–835. 10.3183/npprj-2012-27-05-p828-835.
- Kim, U.-J., Kuga, S., Wada, M., Okano, T., Kondo, T. (2000) Periodate Oxidation of Crystalline Cellulose. *Biomacromolecules* 1(3):488–492. 10.1021/bm0000337.
- Kishimoto, T., Nakatsubo, F. (1998) Non-Chlorine Bleaching of Kraft pulp. V. Participation of Radical Species in Ozonation of Methyl 4-O-Ethyl- β -D-Glucopyranoside. *Holzforschung* 52(2):185–190. 10.1515/hfsg.1998.52.2.185.
- Lewin, M., Ettinger, A. (1969) Oxidation of cellulose by hydrogen peroxide. *Cellul. Chem. Technol.* 3(1):9–20.
- Martinsson, A., Hasani, M., Potthast, A., Theliander, H. (2020) Modification of softwood kraft fibres using H2O2 at mildly acidic conditions. *Cellulose* 27:7191–7202. 10.1007/s10570-020-03245-z.
- Münster, L., Vicha, J., Klofáč, J., Masař, M., Kucharczyk, P., Kuřitka, I. (2017) Stability and aging of solubilized dialdehyde cellulose. *Cellulose* 24:2753–2766. 10.1007/s10570-017-1314-x.
- Saito, T., Isogai, A. (2004) TEMPO-Mediated Oxidation of Native Cellulose. The Effect of Oxidation Conditions on Chemical and Crystal Structures of the Water-Insoluble Fractions. *Biomacromolecules* 5(5):1983–1989. 10.1021/bm0497769.
- Sjöberg, J., Potthast, A., Rosenau, T., Kosma, P., Sixta, H. (2005) Cross-sectional analysis of the polysaccharide composition in cellulosic fiber materials by enzymatic peeling/high-performance capillary zone electrophoresis. *Biomacromolecules* 6(6):3146–3151. 10.1021/bm050471j.
- Theander, O., Westerlund, E. (1986) Studies on dietary fiber. 3. Improved procedures for analysis of dietary fiber. *J. Agric. Food Chem.* 330–336. 10.1021/jf00068a045.
- Zeronian, S.H., Inglesby, M.K. (1995) Bleaching of Cellulose Using Hydrogen Peroxide. *Cellulose* 2:265–272. 10.1007/BF00811817.
- Zhao, H., Heindel, N.D. (1990) Determination of degree of substitution of formyl groups in polyaldehyde dextran by the hydroxylamine hydrochloride method. *Pharm. Res.* 8(3):400–402. 10.1023/A:1015866104055.