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Cellulose degradation in alkaline media upon acidic pretreatment and stabilisation

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ABSTRACT

The present study reports on a revised kinetic model for alkaline degradation of cellulose accounting for primary peeling/stopping reactions as well as for alkaline hydrolysis followed by secondary peeling. Oxalic acid pretreated cotton linters was utilised as the model substrate for the prehydrolysis-soda anthraquinone process. The main emphasis was investigating the effect of end-group stabilising additives such as sodium borohydride (BH), anthraquinone (AQ), and anthraquinone-2-sulphonic acid sodium salt (AQS) on the rates of the yield loss reactions. BH and AQS ensured a cellulose yield gain of 13% and 11%, respectively, compared to the reference. Both stabilisation agents decreased the content of the reducing end groups in the samples, while in the case of AQS stabilisation a 25% increase in carboxyl group content compared to the reference was also observed. As expected, the addition of end group stabilisers resulted in a significant decrease in the peeling-to-stopping rate constants ratio.

1. Introduction

Cellulose is the world's most abundant natural polymeric raw material with a fascinating structure and properties. Wood pulp remains the dominant raw material source for processing cellulose, most of which is used to produce paper and board. Only a small fraction of less than 3% (5 million tonnes in 2010 according to Tappi, 2011) was used for manufacturing regenerated cellulose fibres and films, as well as for synthesising cellulose esters and ethers. The coexisting polymers in lignocellulosic raw materials, hemicelluloses and lignin, are primarily used as an energy source and only in very small amounts isolated for use as chemicals, building blocks and food additives.

However, quite recently for numerous environmental and economic reasons lignocellulosic biomass started to appear more like a complex raw material offering various refinery products. Extensive research has been devoted to developing pretreatments, considered the first step in sequential refining of lignocellulosic. In dissolving pulp production, for example, isolating hemicelluloses with water prehydrolysis could be implemented as a separate stage before alkaline pulping provided that the concomitantly released water insoluble lignin can be separated in a commercially feasible way (ANDRITZ, 2012; Leschinsky, Zuckerstätter, Weber, Patt, & Sixta, 2008a,b; Sixta, Potthast, & Krotschek, 2006). Another challenge of the acidic pretreatment, especially at very high autohydrolysis intensity (*P*-factor), is to avoid hydrolytic depolymerisation of the residual cellulose fraction (Borrega, Tolonen, Bardot, Testova, & Sixta, 2012). Cleavage of glycosidic bonds leads to a dramatic decrease in the degree of polymerisation (DP) and the formation of new reducing end groups (Lin, 1979).

The reducing end group (REG) is a reactive aldehyde carbonyl present at one end of a cellulose molecule comprising high reactivity towards aqueous alkaline conditions. The REGs are involved in two reaction types: stepwise peeling eliminating anhydroglucose units (β-elimination) through the formation of isosaccharinic acid ($E_a = 102.9$ kJ/mol) until the process is terminated by a competing stopping reaction ($E_a = 134.7$ kJ/mol) converting the REG into metasaccharinic acid (MSA) which in turn is stable to a peeling-off reaction (Haas, Hrutfiord, & Sarkanen, 1967). Alkaline hydrolysis ($E_a = 150.2$ kJ/mol), resulting in the cleavage of glycosidic bonds, triggers secondary peeling at the newly created REGs (Lai &

Abbreviations: AQ, anthraquinone; AQS, anthraquinone-2-sulphonic acid sodium salt; BCA, 2,2′-bicinchoninate; BH, sodium borohydride; CL, cotton linters; OA, oxalic acid; REG, reducing end group.

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Sarkanen, 1967). The peeling-off reaction is primarily responsible for the yield loss, whereas alkaline hydrolysis mainly affects the DP of the polysaccharide. After acidic prehydrolysis, the residual polysaccharide fraction is very susceptible to peeling-off reactions in subsequent alkaline cooking, which in turn results in substantial pulp yield loss.

Although the decrease in the DP due to prehydrolysis is irreversible, stabilisation of cellulose REGs against alkaline peeling could decelerate further degradation to a certain extent. Previous studies on the stabilisation of wood carbohydrates in alkaline pulping aiming at increased overall pulp yield have provided promising results. Different stabilisation pathways were reported, namely, oxidation (Lindenfors, 1980), reduction (Lehtaru & Ilomets, 1996) and derivatisation (Clayton & Marraccini, 1966; Nilsson & Östberg, 1968) of the REGs among which oxidation is currently the only industrially viable technique (Sixta et al., 2006).

Stabilisation of REGs via oxidation is carried out by adding anthraquinone (AQ) or its derivatives (sulphur-free alkaline cooking) and polysulfide (kraft cooking). Although AQ is insoluble in water and is used in a dispersed form, anthaquinone-2-sulphonic acid sodium salt (AQS) is an example of a water-soluble derivative. AQ and the derivatives convert the reducing end carbonyls to aldonic acids by reducing the own ring carbonyl groups to hydroxyls (Fleming, Kubes, MacLeod, & Bolker, 1978). The stabilising efficiency of each derivative is thought to be affected by its redox potential (Evstigneev & Shalimova, 1985).

A typical compound for selectively reducing carbonyl groups to alcohols is sodium borohydride (BH). The common application for BH has been found in pulp bleaching through reducing the carbonyl groups responsible for pulp yellowing (Lehtaru & Ilomets, 1996). However, successful application as a pulping additive has also been demonstrated (Copur & Tozluoglu, 2008).

Although numerous stabilisation studies have been performed, the work has mostly focused on the actual effect on cellulose or pulp yield, while comprehensive studies on their cellulose degradation kinetics effects are clearly lacking. However, recent kinetic studies of cellulose degradation in an alkaline environment have primarily been concentrated on radioactive waste disposal of cellulosic materials rather than the fractionation of biomass.

Traditionally, as demonstrated by Haas et al. (1967) pseudo-first-order kinetics of alkaline peeling and stopping can be expressed as a system of equations:

$$\left\{ \frac{dR}{dt} = -k_s R \right. , \tag{1}$$

$$\left\{ \frac{dP}{dt} = k_p R \right. , \tag{2}$$

where P is the mole fraction of peeled-off material, t is the reaction time, k_p and k_s stand for the peeling and stopping reaction rates including chemical and physical stopping, respectively, and R is the mole fraction of the REGs. Eq. (1) can be integrated assuming $t = 0$, $R = R_0$, where R_0 is the mole fraction of the REGs at time 0, yielding *-2pt

$$R = R_0 e^{-k_s t}. \tag{3}$$

By substituting R in Eq. (2) with (3), the differential equation

$$\frac{dP}{dt} = k_p R_0 e^{-k_s t} \tag{4}$$

is obtained. After integrating (4) at $t = 0$, $P = 0$ the equation for the cellulose yield loss fraction results in

$$P = \frac{k_p}{k_s} R_0 (1 - e^{-k_s t}). \tag{5}$$

The kinetics of alkaline hydrolysis was studied by Lai and Sarkanen (1967). Later, Van Loon and Glaus (1997) and Pavasars, Hagberg, Borén, and Allard (2003) expressed the overall carbohydrate yield loss (D) at constant alkali concentration combining peeling, stopping and alkaline hydrolysis (k_h) reactions in (6).

$$D = 1 - \left(1 - \left(\frac{k_p}{k_s} R_0 (1 - e^{-k_s t})\right)\right) e^{-k_h t} \tag{6}$$

This traditional model included the three rate constants typical for cellulose degradation. However, the model did not take into account secondary peeling. To extend the model, a term denoting cellulose degradation resulting from secondary peeling has to be included.

In the present study, an attempt to develop better understanding of cellulose degradation in the simulated conditions of sulphur-free prehydrolysis-soda AQ pulping is made using cotton linters as a model cellulose substrate. Emphasis is placed on investigating stabilisation effects and changes entailed in the cellulose substrate by adding oxidising (AQ and AQS) and reducing (BH) chemicals compared to the reference conditions. Finally, a comprehensive model is applied to simulate the yield loss kinetics of untreated and oxalic acid pretreated cellulose in aqueous alkaline conditions in the presence or absence of REG-stabilisers.

2. Experimental

2.1. Sample preparation

For the experiments cotton linter pulp (CL) was delivered by Milouban (M.C.P) Ltd (Israel), oxalic acid (OA) by Sigma–Aldrich (St. Louis, MO, USA), BH by Acros Organics (Geel, Belgium), Baycel AQ by Kemira Chemie GmbH (Leverkusen, Germany), AQS by Merck Chemicals (Darmstadt, Germany) and filter paper by Macherey-Nagel (Düren, Germany). All chemicals were used in the highest grade available, except when stated otherwise.

All experiments were carried out on CL. CL was grinded in a Wiley mill using a mesh size of 0.5 mm (intrinsic viscosity after grinding 890 ml/g). Dry matter content was determined according to SCAN-C3:78.

CL was pretreated with 0.01 M OA at a 15 ml/g liquid-to-solid ratio, treatment temperature of 110 °C with an isothermal duration of 80 min. Oxalic acid selection was governed by its medium acid strength (pK_{a1} = 1.27 and pK_{a2} = 4.28) and the absence of heteroelements.

Stabilisation of cellulose was performed as an intermediate step (BH only) or in situ during alkaline degradation step. Intermediate treatment with BH was carried out at 70 °C with varied BH concentrations, a liquid-to-solid ratio of 15 ml/g, and isothermal treatment duration after optimisation of 60 min (OA CL-(BH)$_{\mathrm{opt}}$). The BH half-life in aqueous conditions dependent on the pH and the temperature of the reaction was calculated as

$$\log t_{1/2} = \mathrm{pH} - (0.034T - 1.92) \tag{7}$$

according to Mochalov, Shifrin, and Bogonostsev (1964). Hence, pH in the BH treatment stage was adjusted to 13 with NaOH, where the BH half-life of 30.3 h at 70 °C was acceptable for the selected treatment time.

Alkaline degradation trials were carried out at a temperature of 160 °C, a liquid-to-solid ratio of 40 ml/g, an alkali concentration of 20 g/l, and the addition of dispersed 0.1 g/l AQ, except for the trials with AQS, trials with varied AQ concentrations and selected trials with BH. Fixed isothermal treatment duration of 64 min was applied when optimisation of stabilisation chemicals charge was performed. In situ stabilisation was attempted by adding water-dispersed Baycel AQ containing 45% AQ and 5% surfactant (OA CL-AQ$_{\mathrm{opt}}$), AQS (OA CL-AQS$_{\mathrm{opt}}$), and BH (OA CL-BH$_{\mathrm{opt}}$), where opt denotes the optimisation of stabilisation agent concentrations.

The proposed alkaline degradation conditions resemble soda-anthraquinone pulping conditions in a wood-based system except for the high liquid-to-solid ratio which was selected to keep the alkali concentration largely unaffected throughout the reaction which is a prerequisite for a kinetic study.

The kinetic study included the following alkaline degradation time series at 125 °C and 160 °C with process durations of up to 70 h and 5 h, respectively:

1. untreated CL (CL)
2. acid pretreated CL (OA CL)
3. acid pretreated CL with in situ BH stabilisation (OA CL-BH)
4. acid pretreated CL with in situ AQS stabilisation (OA CL-AQS)

Acid pretreatment of CL was carried out in the rotating air bath reactor with six 2500 ml stainless steel autoclaves. All stabilisation and alkaline degradation experiments were performed in a rotating oil bath reactor with 8 bombs of 220 ml each. After the experiments were completed, samples were washed on filter paper MN 617 until neutral and dried in ambient conditions. The liquid phase after alkaline degradation was collected and stored for further analyses.

2.2. Analytical procedures

Liquid alkaline samples were neutralised with 0.5 M H_2SO_4 to pH 6–8 and cellulose yield loss was measured in the liquid phase with total organic carbon (TOC) analysis. The TOC values were recalculated into cellulose yield loss with the consideration of the organic additives (AQ and AQS) concentration assuming that no adsorption took place on the CL surface. The residual alkali content of the undiluted samples was determined with an automatic titrator according to SCAN-N 33:94.

Viscosity of the solid residue in cupriethylenediamine (CED) was determined, and the viscosity–average degree of polymerisation (DP_v) was calculated according to SCAN-CM 15:99. Sulphur content of the CL samples treated with AQS was determined by combustion of approximately 50 mg of the sample in an oxygen environment in a Schöniger flask containing 25 ml water and 0.5 ml of 30% hydrogen peroxide, followed by 45 min of absorption. The resulting solution was analysed for sulphate anions concentration by ion chromatography according to SCAN-CM 57:99.

The REGs content of the solid samples was evaluated with the BCA (bicinchoninic acid) method and fluorescence labelling combined with gel permeation chromatography (GPC). Evaluation of the REGs in cellulose substrates with the BCA method was reported by Kongruang, Han, Breton, and Penner (2004). A purple water-soluble complex of two molecules of bicinchoninic acid chelating with a single Cu(I) ion is formed. The complex formation is quantified by measuring light absorption at 562 nm. Cu(I) ions originate from the reduction of Cu(II) ions in $CuSO_4$ by cellulose REGs. The working solution for the determinations was prepared as described by Garcia, Johnston, Whitaker, and Shoemaker (1993) using 2,2′-bicinchoninate solid supplied by Pierce (Rockford, USA), sodium carbonate, L-serine and copper (II) sulphate pentahydrate by Sigma–Aldrich (St. Louis, MO, USA), and sodium hydrogen carbonate by VWR (Fontenay sous Bois, France). Quantification of REGs by fluorescence labelling and GPC (the CCOA method) was carried out as described by Röhrling et al. (2002). The fluorescence labelling of cellulose was performed with CCOA ([2-(2-aminooxyethoxy)ethoxy]amide). The GPC system with multiple-angle laser light scattering detection (MALLS), fluorescence and refractive index detector was utilised to quantify and record the distribution of the REGs. Both methods quantify the total amount of carbonyl groups in the substrate; therefore, an assumption that the content of the carbonyl groups rather than at the reducing ends is negligibly small had to be made.

Carboxyl groups content was measured using the methylene blue adsorption method discussed by Davidson (1948). A 300 mg/l methylene blue solution was prepared, and a calibration using different dilution factors was performed by measuring extinction at 665 nm. Cellulose substrate in the amount corresponding to 40–60% methylene blue adsorption was placed in a flask together with 25 ml of methylene blue and 25 ml of buffer solution (pH 8.5, (1.24 g H_3BO_3 + 2.1 ml 1 N NaOH)/1 l water) and was kept in a water bath at 20 °C for 60 min. The liquid fraction was separated on a glass G3 filter, and an aliquot of 2 ml was placed into a 100 ml volumetric flask together with 10 mL of 0.1 N HCl. The extinction of the resulting solution was measured. All glassware except for the volumetric flasks was treated overnight with methylene blue solution before the experiment. The content of carboxyl groups was calculated as the amount of adsorbed methylene blue divided by the molar mass of methylene blue and related to the sample weight.

Cellulose crystallinity and crystallite dimensions were determined with wide-angle X-ray scattering (WAXS) for the samples after 3 h (160 °C) and 46 h (125 °C) of alkaline treatment. The samples were pressed in metal rings (thickness 1 mm) and measured using Cu Kα radiation (wavelength 1.541 Å), described in more detail by Tolonen et al. (2011). Additionally, the 0 0 4 reflection of cellulose Iβ ($2\theta = 34.5^\circ$) was measured in symmetrical transmission geometry, using a four-circle diffractometer that consisted of a four-circle goniometer (420/511, Huber), an X-ray generator (ID 3003, Seifert), a sealed X-ray tube with a Cu anode, a ground and bent Ge monochromator, and a NaI(Tl) scintillation counter.

The cross-sectional crystal dimensions (from reflections 1–10, 1 1 0 and 2 0 0) were calculated by fitting five Gaussian functions to the intensity together with an amorphous background (sulfate lignin) between 2θ values from 12° to 26°. The 0 0 4 reflection was fitted with a parabola on the top of the peak and two straight lines on its sides, assuming a linear background. In both cases the crystal size was computed using the Scherrer equation with the instrumental broadening taken into account (Leppänen et al., 2009). For the calculation of crystallinity, a total of 37–40 Gaussian functions together with the amorphous background were fitted to model the experimental intensity on a 2θ range extending from 10° to 45° and the crystallinity was calculated based on the ratio of the areas below the amorphous fit and the measured intensity.

2.3. Kinetic modelling

A model taking into account secondary peeling, namely, peeling at the REGs created as a result of hydrolysis was developed. The evaluation of the rate constants was performed by fitting the experimental yield loss time curves to the traditional (Eq. (6)) and the suggested model using the FindFit function in Mathematica software.

3. Results and discussion

3.1. Oxalic acid treatment

Cellulose yield loss upon acid pretreatment accounted for approximately 3% (Fig. 1a) due to dissolution of the small low-molecular-weight fractions. Subsequent treatment in alkali, however, involved peeling at the inherent and newly created REGs and, consequently, fast dissolution of an additional 15% of the cellulose during the heat-up period. Prolonged exposure to alkali caused further yield losses, however, at a lower rate. As expected, cellulose DP_v was affected by acid prehydrolysis that was reflected in a pronounced DP_v decrease (Fig. 1b). The DP_v remained almost constant in subsequent alkaline treatment since the β-elimination has only a minor effect on the polymer chain length of the residue and the rate

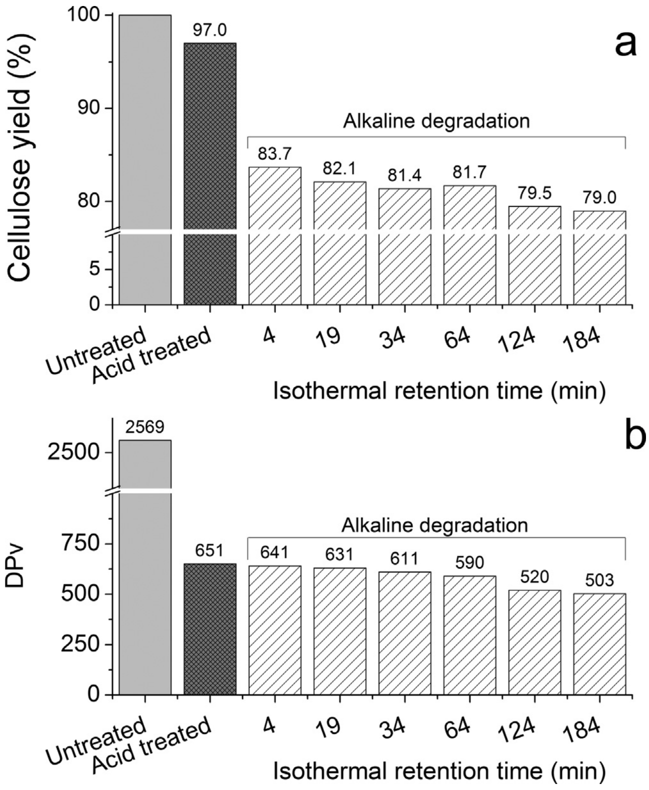

Fig. 1. Effect of oxalic acid pretreatment and alkaline degradation on cellulose yield (a) and DP (b). Pretreatment with 0.01 M oxalic acid, 15 ml/g, 110 °C. Alkaline degradation conditions: 160 °C, 40 ml/g, NaOH 20 g/l, AQ 0.1 g/l.

of alkaline hydrolysis was rather low at the studied temperature (Table 3).

3.2. *Evaluation of the stabilisation effects of different chemicals*

3.2.1. *Intermediate stabilisation with BH*

Adding BH in a concentration of 0.2 mol/l (7.6 g/l) for 12 h in a separate reaction between OA and the alkaline treatments resulted in an overall 9% yield gain compared to the unstabilised case (not shown here). In subsequent optimisation trials, comparable yield gains were observed at substantially milder conditions, such as a BH concentration of 0.02 mol/l (0.76 g/l) for 0.5 h (Fig. 2a, OA CL – $(BH)_{opt}$). However, BH applied at pH 13 and 70 °C in an intermediate step was also accompanied by alkaline peeling, which contributed to the overall yield loss.

3.2.2. *In situ stabilisation with BH*

The addition of 0.02 mol/l of BH in situ in the alkaline degradation stage instead of performing a separate treatment resulted in a superior yield gain of 13% (OA CL-BH_{opt} in Fig. 2a). Further, addition of AQ in BH in situ experiments was motivated by the assumption that in the case of sulphur-free alkaline delignification of lignocellulosic material a nucleophile will be required. Therefore, all further in situ experiments with BH were performed with the addition of 0.1 g/l of AQ. As demonstrated by OA CL-$BHAQ_{opt}$ in Fig. 2, the addition of AQ reduced the stabilisation effect of BH. The yield gain at the addition of 0.02 mol/l BH (0.76 g/l) was approximately 4% lower in the presence of AQ compared to the pure BH stabilisation. This effect may be explained by a competing reaction occurring between BH and the carbonyl groups of AQ confirmed by the colour change from light yellow to red upon the heat-up of the alkali-AQ-BH mixture. As other reasons for reduced stabilisation effect, competition in oxidation and reduction at the REGs are not excluded.

3.2.3. *In situ stabilisation with AQ and AQS*

Performing alkaline degradation with increased AQ concentrations (OA CL-AQ_{opt} in Fig. 2a) resulted in yields comparable to those of intermediate stabilisation with BH. However, AQS (OA CL-AQS_{opt} in Fig. 2a) had a similar effect at much lower charges and reached its maximum efficiency at about 1 g/l with a yield gain of 11%. The differences between AQ and its derivative can mainly be attributed to the water solubility of the latter and, second, to the difference in redox potentials (Evstigneev & Shalimova, 1985). Since AQ and AQS are bulky molecules, it was questioned whether the yield increase could be caused by their retention in cellulosic material. The hypothesis was investigated by quantifying the sulphur content in the sample after alkaline degradation with the addition of AQS. The results revealed that only 0.0034% of the total yield gain of 10% was represented by AQS remaining in the sample. On a molar basis, AQS showed a substantially higher stabilisation rate than BH, while for AQ it was on a comparable level. As shown in Fig. 2b, the addition of AQS achieved an effect similar to that of BH at an eight times lower molar concentration. This may be attributed to the regeneration possibility through reoxidation of reduced AQ and its derivatives even in pure carbohydrate systems (Gratzl & Chen, 1993) while BH is irreversibly consumed upon the transfer of hydride anions to the carbonyl groups (Adams, Gold, & Reuben, 1977). Additionally, low stability of BH in aqueous conditions also affects the extent of stabilisation.

The kinetic study of in situ stabilisation required selection of optimal additives concentrations. The BH and AQS concentrations of 0.76 g/l (0.02 mol/l) and 0.7 g/l (0.0023 mol/l), respectively, were found to ensure similarly high cellulose yield of 90–92% after alkaline degradation which is 9–11% higher than for the reference.

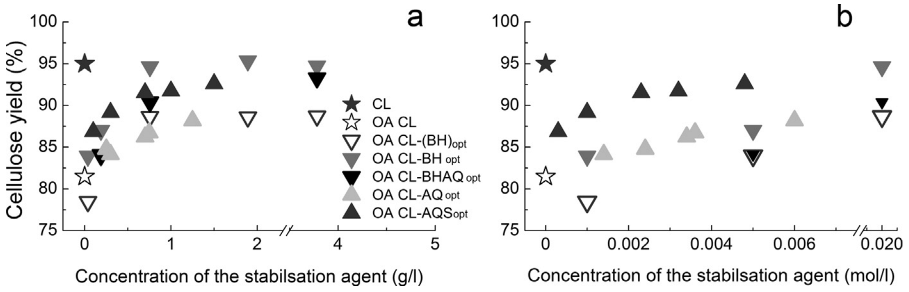

Fig. 2. Effect of different additives on the yield of the acidic pretreated cotton linters after alkaline degradation as a function of concentration expressed as g/l (a) and mol/l (b). Alkaline degradation conditions: 160 °C, 40 ml/g, NaOH 20 g/l, AQ 0.1 g/l (only in OA CL-(BH)opt and CL-$BHAQ_{opt}$), 64 min isothermal treatment time. CL and OA CL correspond to the yields after alkaline degradation of, respectively, untreated and pretreated with OA cotton linters without stabilisation. OA CL-(BH)opt corresponds to alkaline degradation of CL pretreated with OA and treated with BH in a separate stage at 70 °C, 15 ml/g, isothermal treatment duration 60 min and varied BH concentrations. OA CL-BHopt, OA CL-$BHAQ_{opt}$, OA CL-AQ_{opt}, and OA CL-AQS_{opt} correspond to alkaline degradation of CL pretreated with OA with in situ addition of the corresponding stabilisation chemicals.

Table 1
Comparison of the reducing end groups' quantification methods for the CL before alkaline degradation.

Sample	Content of reducing end groups, μmol/g			Content of carboxyl groups, μmol/g
	BCA method	CCOA	Reciprocal of DP_n	
Cotton linters	3.62	3.70	9.01	8.6
Cotton linters pretreated with 0.01 M oxalic acid, 15 ml/g, 110 °C	7.72	12.9	19.2	10.5

3.3. Cellulose functionalities and supramolecular properties

The content of the REGs in the untreated and acid treated CL before alkaline degradation determined using three different methods confirmed the notable formation of the REGs through hydrolytic cleavage of the glycosidic bonds (Table 1). As expected, the reciprocal value of cellulose DP_n had the highest values; however, it can be used only as an estimate of the REG content since it is based on the assumption that every cellulose molecule carries an REG. In the BCA method, similarly to the copper number, the carbonyls are quantified indirectly and the mechanism is not fully understood (Röhrling et al., 2002), while the CCOA method is a direct measure of the total number of carbonyl groups including aldehydes (REG) and ketones. Assuming that the share of ketones in the untreated and treated CL samples is negligibly small, the CCOA method is considered the most reliable for quantifying the REGs. Thus, the results from this method were utilised in further kinetic study.

A rapid decrease in the carbonyl groups content (the BCA method) upon alkaline degradation in Fig. 3a confirmed that practically all primary peeling and stopping and resulting formation of MSA occur in the initial treatment phase. In the presence of stabilisation agents, the conversion of the REG to the respective functionalities (alditol or aldonic acid) was reflected in the lowest (under 1 μmol/g) REGs content.

Due to non-specific adsorption of methylene blue (Bohrn et al., 2006) the obtained carboxyl group content (Fig. 3b) is likely to be slightly overestimated. This is also reflected in the sum of the REGs and carboxyl groups higher than the reciprocal DP_n (Table 1). As anticipated, the conversion of the REGs into aldonic acid groups upon AQS stabilisation resulted in a notable increase in carboxyl group content (up to 22 μmol/g). The contribution of MSA to the carboxyl group content as a result of chemical stopping was highest for OA CL (Fig. 3b). The summative content of the carbonyl and carboxyl groups similarly to the reciprocal DP_n values in Fig. 3c increased during the course of alkaline degradation as a result of alkaline hydrolysis. In the case of BH stabilisation, however, a great part of the REGs is converted to alditols which is reflected in a significant gap between the reciprocal DP_n values and the sum of carbonyl or carboxyl group content.

The WAXS investigation (Table 2) did not reveal any effect of the stabilisation agent addition on the crystallinity of cellulose. The OA pretreatment is apparently too mild to cause removal of the amorphous material. A modest increase in cellulose crystallinity from 62% to 65% (160 °C and 125 °C) was observed solely as a result of the alkaline treatment where the removal of the amorphous cellulose obviously occurs. A minor increase in crystallite length (B_{004}) was noticed in the case of alkaline degradation, which could be attributed to the increased chain mobility caused by the removal of cellulosic material and resulting in cellulose crystallisation in the chain direction (Leppänen et al., 2009). The cross-sectional crystal dimensions (B_{1-10}, B_{110}, B_{200}) remained practically unchanged.

3.4. Kinetic study

A kinetic model for cellulose degradation in alkaline conditions taking into account secondary peeling, namely, peeling at the REGs created as a result of hydrolysis can be expressed by the following system of differential equations:

$$\begin{cases} \dfrac{dR}{dt} = -k_s R + k_h(\Gamma_0 - P - H) \\ \dfrac{dP}{dt} = k_p R \\ \dfrac{dH}{dt} = k_h(\Gamma_0 - P - H) \end{cases}$$

where Γ_0 stands for the amount of initial material, R for the mole fraction of the REGs, P the mole fraction of peeled off material, and, finally, H the mole fraction of degraded material through hydrolysis. The reaction rate constant for stopping is denoted k_s, for peeling k_p and for hydrolysis k_h. Eq. (8) states that the decrease in REGs due to the stopping reaction is proportional to the amount of REGs and the increase due to hydrolysis is proportional to the amount of non-degraded material. Eq. (9) expresses that the material is being peeled off at a rate proportional to the amount of REGs. According to Eq. (10), the degradation rate due to hydrolysis is proportional to the amount of non-degraded material. The messages of Eqs. (8) and (10) are coherent; when hydrolysis removes one element from a chain, only one of the new ends becomes an REG. To determine the integration constants arising in the solution of Eqs. (8)–(10), the

Table 2
Changes in cellulose crystallinity and crystal dimensions induced by acidic and alkaline treatments and combination thereof.

	Crystallinity (%)	Crystallite dimensions (nm)			
		B_{1-10}	B_{110}	B_{200}	B_{004}
CL 0	62	5.3	6.5	6.4	20
OA CL 0	63	5.2	6.4	6.4	n.m.[a]
CL 160 °C[b]	65	5.3	6.6	6.6	n.m.[a]
OA CL 160 °C[b]	66	5.2	6.4	6.4	23
OA CL-BH 160 °C[b]	65	5.2	6.4	6.4	21
OA CL-AQS 160 °C[b]	65	5.2	6.3	6.3	n.m.[a]
OA CL 125 °C[c]	65	5.3	6.5	6.4	n.m.[a]

[a] Not measured.
[b] 3-h alkaline degradation at 160 °C.
[c] 46-h alkaline degradation at 125 °C.

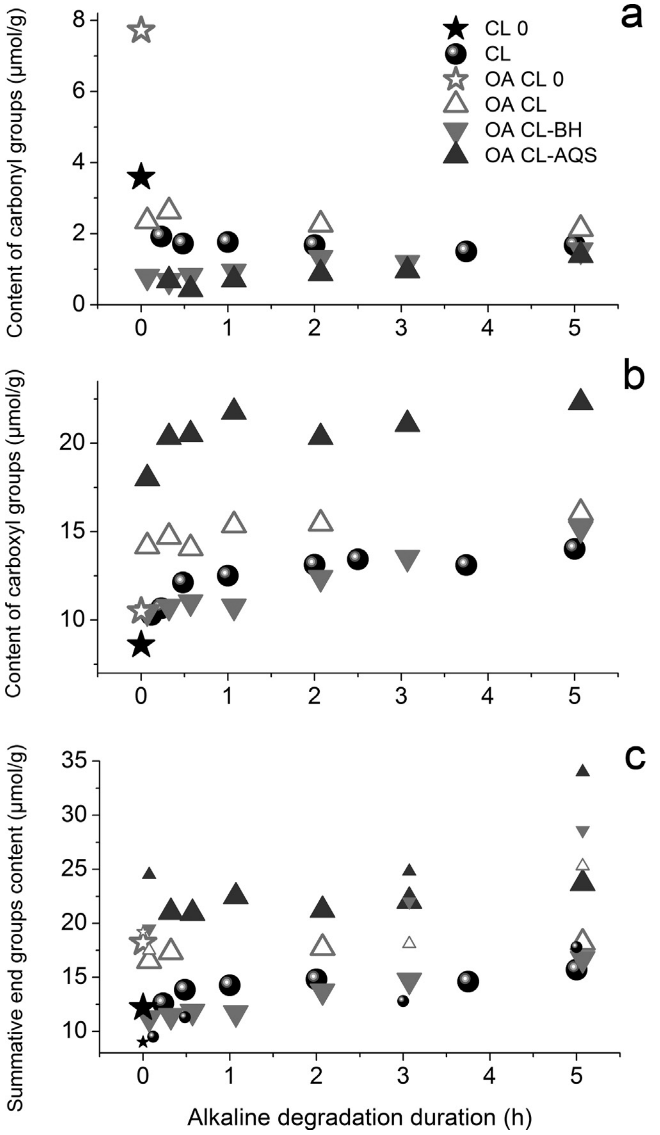

Fig. 3. Content of REGs determined by the BCA method (a), carboxyl groups (b) and a sum of REGs and carboxyl groups (c) in cotton linters before (CL 0 and OA CL 0) and after alkaline degradation. Alkaline degradation conditions: 160 °C, 40 ml/g, NaOH 20 g/l, AQ 0.1 g/l. Smaller symbols in (c) represent reciprocal values of cellulose DP_n.

initial values are set $P(0) = H(0) = 0$ and $R(0) = \rho_0 \Gamma_0$, where ρ_0 is the initial portion of REGs.

The system of Eqs. (8)–(10) can be solved with the DSolve function of the Wolfram Mathematica software. The amount of degraded material $D = P + H$ has to be determined. After some tedious algebra on the solution given by Mathematica we arrive at:

$$D = \Gamma_0 \left(1 - \left[\frac{1}{2} + \gamma\right] \exp\left(-\left(\alpha + \beta\right) t\right) - \left[\frac{1}{2} + \gamma\right] \times \exp\left(\left(\alpha - \beta\right) t\right)\right), \tag{11}$$

with

$$\begin{cases} \alpha = \frac{1}{2}\sqrt{(k_s - k_h)^2 - 4k_h k_p} \\ \beta = \frac{1}{2}(k_h + k_s) \\ \gamma = \dfrac{k_h + 2\rho_0 k_p - k_s}{2\sqrt{(k_s - k_h)^2 - 4k_h k_p}} \end{cases} . \tag{12}$$

To solve a system like Eqs. (8)–(10) manually, the system is transformed into one higher-order differential equation. In the present case, it suffices with a second-order differential equation even if there are three equations in the system. Taking the derivative on both sides of Eq. (8), we obtain:

$$\frac{d^2R}{dt^2} = -k_s \frac{dR}{dt} - k_h \left(\frac{dP}{dt} + \frac{dH}{dt}\right). \tag{13}$$

Inserting Eqs. (9) and (10) into (13), we get:

$$\frac{d^2R}{dt^2} = -k_s \frac{dR}{dt} - k_h \left(k_p R + k_h (\Gamma_0 - P - H)\right). \tag{14}$$

Then multiplying Eq. (8) with k_h, adding it to (14) and rearranging terms give:

$$\frac{d^2R}{dt^2} + (k_s + k_h) \frac{dR}{dt} + k_h \left(k_p + k_s\right) R = 0. \tag{15}$$

Eq. (15) is a second-order homogeneous differential equation with constant coefficients. The solutions of the characteristic equation are: $-\beta \pm \alpha$, with the notation of (12). Assuming that α is real and positive, the solution to (15) is:

$$R = C_1 \exp\left(\left(-\beta + \alpha\right) t\right) + C_2 \exp\left(\left(-\beta - \alpha\right) t\right), \tag{16}$$

where C_1 and C_2 are integration constants. Inserting (16) into (9) and solving the equation, we obtain:

$$P = C_3 + k_p \left(C_1 \frac{\exp((-\beta+\alpha)t)}{-\beta+\alpha} + C_2 \frac{\exp((-\beta-\alpha)t)}{-\beta-\alpha}\right), \tag{17}$$

with a new integration constant C_3. After inserting (16) and (17) into (8), H can be calculated:

$$H = \Gamma_0 - C_3 - \left(\frac{(\alpha-\beta+k_s)}{k_h} + \frac{k_p}{\alpha-\beta}\right) C_1 \exp\left(\left(\alpha - \beta\right) t\right) + \left(\frac{(\alpha+\beta-k_s)}{k_h} + \frac{k_p}{\alpha+\beta}\right) C_2 \exp\left(-\left(\alpha + \beta\right) t\right) \tag{18}$$

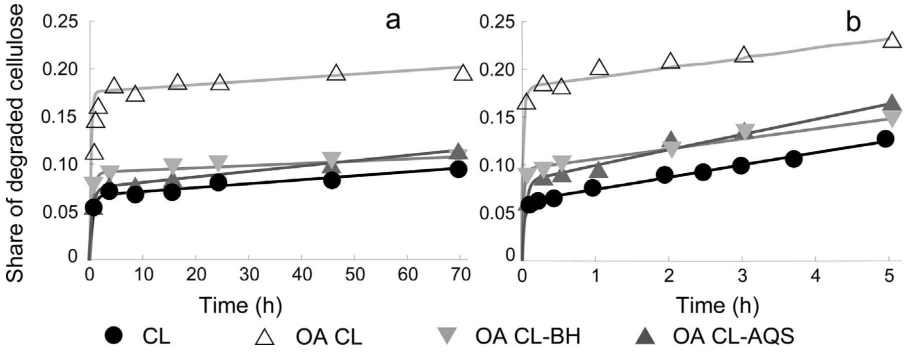

Fig. 4. Data fits to the developed model for alkali degradation at 125 °C (a) and 160 °C (b), 40 ml/g, NaOH 20 g/l, AQ 0.1 g/l, BH and AQS concentrations in the respective series 0.76 and 0.7 g/l.

The integration constants can be determined with the earlier mentioned initial conditions. After some lengthy calculations, Eq. (11) is reached for the degraded material.

Kinetic analysis of the date series yielded fits (Fig. 4) with the high coefficients of determination ($R^2 > 0.99$) given in Table 3. At the same time, large relative standard errors inherent in the rate constant estimates of the developed (Eqs. (11) and (12)) and traditional (Eq. (6)) models (Table 3), particularly, for peeling and stopping, indicated that almost equally good fits could be obtained for a wide range of parameter values. The reasons seem to be the small number of available data points during the initial fast degradation and the linear correlation between the peeling and stopping parameters. Because of this correlation, the ratio between the estimated reaction rate constants is less prone to error than the individual constants.

Comparison of the two models revealed only minor differences for the peeling and stopping rate values. However, the hydrolysis rate constants calculated according to the developed model were by two orders of magnitude lower than those in the traditional model since the latter has significance for the amount of the remaining cellulose only through creating new REGs. Despite the different underlying mechanisms and the analytic expressions, the curves fitted to the data were almost identical for the two models.

To support the developed model an example evaluation of first-order cellulose chain scission kinetics closely corresponding to alkaline hydrolysis was performed graphically according to Eq. (19).

$$\frac{1}{DPv_t} - \frac{1}{DPv_0} = k_{CS}t, \tag{19}$$

where k_{CS} is the rate constant for hydrolytic chain scission, DPv_t is DPv at time t of alkaline degradation, DPv_0 is the starting DPv and $\frac{1}{DPv_t} - \frac{1}{DPv_0}$ is the number of chain scission per anhydroglucose unit at time t. Based on the DPv values in Fig. 1b, a calculation of k_{CS} for OA pretreated CL was performed and a value of $1.8 \times 10^{-4}\,h^{-1}$ was obtained which resembled the k_h value of $1.4 \times 10^{-4}\,h^{-1}$ obtained with the developed model rather than $130 \times 10^{-4}\,h^{-1}$ with the traditional model.

Two distinct yield loss phases are identified in Fig. 4. The initial phase is controlled by the rapid primary peeling-off reaction until fully terminated by chemical and physical stopping. The second phase represents slow degradation triggered by alkaline hydrolysis causing secondary peeling. According to the proposed model, all cellulose will be degraded after 20,000 and 400 h at 125 °C and 160 °C, respectively.

In both models, the peeling rate constant is sensitive to the initial content of the REGs. Since the untreated CL and CL after the acid pretreatment carry different initial amounts of REGs, the precision of the REGs quantification is determinative. Table 3 reveals a significant drop in the peeling-to-stopping ratios when BH or AQS was added to the alkaline reaction liquor, which confirms the stabilisation of cellulose against endwise degradation. The peeling-to-stopping ratios remained unchanged when the temperature was increased from 125 to 160 °C, except for AQS stabilisation. Accordingly, the estimated activation energies (E_a) (Table 3) were on the same magnitude for peeling and stopping unlike in the published data ($E_{ap} = 102.9$, $E_{as} = 134.7$ kJ/mol). However, due to the limited number of temperature points presented in this study the E_a values are only estimative. To improve the precision additional experiment series would be necessary.

While the alkaline treatments of the unstabilised CL, unstabilised OA CL and BH stabilised OA CL revealed decreasing peeling-to-alkaline hydrolysis (k_p/k_h) ratios with increasing temperature, the opposite occurred for the alkaline cooking of the AQS stabilised OA CL (Table 3). The magnitude of the k_h values in the AQS stabilisation series was the largest among the other series.

Table 3
Rate constants and standard errors for reactions of cellulose in an alkaline environment calculated by applying the traditional model (Eq. 6) (values in parentheses) and the further developed model (Eqs. (11) and (12)). Activation energies calculated of the respective reactions calculated based on two temperatures are presented in italics.

	k_p, h^{-1}		k_s, h^{-1}		$k_h \times 10^4$, h^{-1}		k_p/k_s		$k_p/k_h \times 10^{-7}$		Coefficient of determination R^2	
Reaction temperature, °C	125	160	125	160	125	160	125	160	125	160	125	160
Cotton linters	200 ± 35 (199 ± 35)	2719 ± 1232 (2696 ± 1231)	1.8 ± 0.3 (1.8 ± 0.3)	26 ± 13 (26 ± 13)	0.040 ± 0.007 (4.5 ± 0.6)	1.3 ± 0.1 (140 ± 9)	111 (111)	105 (104)	5.0 (0.044)	2.1 (0.019)	0.999	0.999
Activation energy, kJ/mol	*106.7*		*109.1*		*142.3 (140.5)*							
CL treated with oxalic acid - no stabilisation	327 ± 26 (327 ± 26)	3172 ± 608 (3166 ± 607)	3.9 ± 0.4 (3.9 ± 0.4)	37 ± 7 (37 ± 7)	0.053 ± 0.016 (4.6 ± 1.2)	1.4 ± 0.3 (130 ± 21)	84 (84)	86 (85)	6.2 (0.071)	2.2 (0.024)	0.999	0.999
Activation energy, kJ/mol	*92.9*		*92.0*		*133.8 (136.6)*							
- stabilisation with BH	83 ± 13 (83 ± 13)	1899 ± 745 (1893 ± 744)	1.9 ± 0.3 (1.9 ± 0.3)	41 ± 17 (41 ± 17)	0.059 ± 0.019 (2.6 ± 0.8)	2.5 ± 0.5 (120 ± 17)	44 (44)	46 (46)	1.4 (0.032)	0.75 (0.016)	0.999	0.998
Activation energy, kJ/mol	*127.9*		*125.5*		*153.1 (156.6)*							
- stabilisation with AQS	29 ± 10 (29 ± 10)	697 ± 173 (688 ± 173)	1.1 ± 0.4 (1.1 ± 0.4)	17 ± 5 (17 ± 5)	0.32 ± 0.07 (9.3 ± 1.4)	4.5 ± 0.7 (190 ± 22)	26 (26)	41 (40)	0.09 (0.0031)	0.15 (0.0036)	0.995	0.997
Activation energy, kJ/mol	*129.9*		*111.9*		*108.0 (123.3)*							

The mechanism underlying this behaviour could be triggered by the oxidation of primary hydroxyl groups at C6 rendering the glycosidic bond adjacent to the respective anhydroglucose unit more reactive towards alkaline hydrolysis (Meller, 1960). Interestingly, the k_h values, obtained with the revised process model (Eqs. (11) and (12)), for BH stabilisation were also higher compared to the unstabilised alkaline treatments (Table 3). Following the findings of Pavasars et al. (2003), this may be attributed to the prevailing higher alkali concentrations during the reaction (Table A.3) owing to the generation of significantly lower amounts of acids during the endwise degradation and the hydrolysis of BH.

3.5. *Outlook*

Since the amount of alkali consumed during the course of alkaline degradation was not accounted for in kinetic modelling, development of a model including the dependency of the alkali concentration is a subject of further investigations. Besides, the focus of future activities should be the effect of the process parameters (alkali concentration) and stabilisation-associated functionalities introduced along the cellulose chain on the degradation kinetics.

In a commercial wood-based system, where cellulose is shielded by other components, less dramatic changes in the cellulose macromolecular properties caused by prehydrolysis and alkaline treatment are expected. Interaction of stabilisation chemicals with other wood components for example preferred stabilisation of hemicelluloses in the residue may weaken the stabilisation effect on cellulose and reactions with lignin may affect delignification.

4. Conclusions

1. Oxalic acid pretreatment of CL severely affected the DP which in turn resulted in a yield loss of 18% after alkaline treatment (160 °C, 65 min, 20 g/l NaOH) compared to only 5% yield loss for the untreated CL.
2. The yield loss initiated by the acid pretreatment could be largely compensated by the addition of stabilisers oxidising the REGs (0.0025 mol/l AQS: 8% yield loss) or by reducing them (0.02 mol/l BH: 6% yield loss).
3. Addition of AQS yielded a cellulosic material with a high content of 22 μmol/g of carboxyl groups, while stabilisation with BH resulted in a generally low content of carboxyl (11–13 μmol/g) and carbonyl groups (0.5–1 μmol/g) due to the conversion of REGs to alditols.
4. No effect of stabilisation agents on cellulose supramolecular properties was observed. Only alkaline degradation resulted in a minor increase in crystallinity at 160 °C due to the removal of the amorphous cellulose.
5. The applied kinetic model accounted for all known alkaline-induced loss reactions including secondary peeling. It also clearly elucidated the effect of the stabilising additives through the decrease of the peeling-to-stopping rate constant ratios and the increase in the hydrolysis rate constant.

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Appendix A.

See Tables A1–A3.

Table A1

Effect of different additives on the yield of acidic pretreated cotton linters after alkaline degradation as a function of concentration. Alkaline degradation conditions: 160 °C, 40 ml/g, NaOH 20 g/l, AQ 0.1 g/l. Cellulose yield no pretreatment and no stabilisation and OA pretreatment and no stabilisation was 95% and 82%, respectively.

Stabilisation series		Stabilisation effect					
OA CL-$(BH)_{opt}$	Concentration of BH	g/l	3.8	1.9	0.76	0.19	0.038
		mol/l	0.1	0.05	0.02	0.005	0.001
	Cellulose yield	%	88.7	88.6	88.7	84.0	78.5
OA CL-BH_{opt}	Concentration of BH	g/l	3.8	1.9	0.76	0.19	0.038
		mol/l	0.1	0.05	0.02	0.005	0.001
	Cellulose yield	%	94.7	95.3	94.6	87.0	83.9
OA CL-$BHAQ_{opt}$	Concentration of BH	g/l	3.8	–	0.76	0.19	–
		mol/l	0.1	–	0.02	0.005	–
	Cellulose yield	%	93.3	–	90.4	84.1	–
OA CL-AQ_{opt}	Concentration of AQ	g/l	1.25	0.75	0.7	0.3	0.25
		mol/l	0.006	0.0036	0.0034	0.0014	0.0024
	Cellulose yield	%	88.2	86.7	86.2	84.1	84.8
OA CL-AQS_{opt}	Concentration of AQS	g/l	1.5	1	0.7	0.3	0.1
		mol/l	0.0048	0.0032	0.0023	0.001	0.0001
	Cellulose yield	%	92.6	91.7	91.5	89.2	86.9

Table A2
Content of REGs determined by the BCA method, carboxyl groups and reciprocal DP$_n$ in cotton linters after alkaline degradation. Alkaline degradation conditions: 160 °C, 40 ml/g, NaOH 20 g/l, AQ 0.1 g/l.

Time, h	0.12	0.23	0.48	1	2	2.5	3	3.75	5
Cotton linters									
Carbonyl groups content (μmol/g)	–	1.92	1.72	1.76	1.68	–	–	1.50	1.68
Carboxyl groups content (μmol/g)	10.3	10.7	12.1	12.5	13.1	13.4	–	13.1	14.0
Reciprocal DP$_n$ (μmol/g)	9.5	–	11.3	–	–	–	12.8	–	17.8
Time, h	0.07	0.32	0.57	1.07	2.07	–	3.07	–	5.07
CL treated with oxalic acid									
No stabilisation									
Carbonyl groups content (μmol/g)	2.35	2.63	–	–	2.26	–	–	–	2.14
Carboxyl groups content (μmol/g)	14.2	14.7	14.1	15.4	15.4	–	–	–	16.1
Reciprocal DP$_n$ (μmol/g)	17.5	–	–	–	–	–	18.1	–	25.3
Stabilisation with BH									
Carbonyl groups content (μmol/g)	0.797	0.678	0.822	0.937	1.33	–	1.18	–	1.54
Carboxyl groups content (μmol/g)	10.4	10.8	11.0	10.8	12.4	–	13.5	–	15.2
Reciprocal DP$_n$ (μmol/g)	19.5	–	–	–	–	–	22.0	–	28.6
Stabilisation with AQS									
Carbonyl groups content (μmol/g)	–	0.684	0.430	0.704	0.879	–	0.964	–	1.39
Carboxyl groups content (μmol/g)	18.0	20.3	20.5	21.8	20.3	–	21.1	–	22.3
Reciprocal DP$_n$ (μmol/g)	24.5	–	–	–	–	–	24.8	–	34.0

Table A3
Yield loss data used for kinetic study and residual alkali in the reaction mixture. The measured initial [OH$^-$] was 18.2 g/l compared to theoretical 20 g/l.

125 °C

Time, h	0.25	0.5	1	4	8	16	24	46	70
Cotton linters									
Yield loss	–	–	0.056	0.072	0.067	0.071	0.081	0.083	0.098
Residual alkali, g/l	–	–	16.3	15.5	15.1	–	14.8	–	14.6
CL treated with oxalic acid									
No stabilisation									
Yield loss	0.114	0.148	0.162	0.184	0.175	0.187	0.187	0.197	0.197
Residual alkali, g/l	15.5	15.0	14.4		13.6	14.0	13.7	13.6	13.8
Stabilisation with BH									
Yield loss	–	–	0.078	0.087	–	0.097	0.101	0.104	0.105
Residual alkali, g/l	–	–	16.2	16.0	–	15.5	15.4	15.3	–
Stabilisation with AQS									
Yield loss	–	–	0.039	0.053	0.061	0.079	–	0.103	0.111
Residual alkali, g/l	–	–	15.8	15.1	15.0	14.7	–	14.7	14.7

160 °C

Time, h	0.12	0.23	0.48	1	2	2.5	3	3.75	5
Cotton linters									
Yield loss	0.060	0.065	0.064	0.078	0.092	0.093	0.098	0.105	0.128
Residual alkali, g/l	16.7	15.7	15.6	15.4	14.7	–	–	13.3	12.8
Time, h	0.07	0.32	0.57	1.07	2.07	–	3.07	–	5.07
CL treated with oxalic acid									
No stabilisation									
Yield loss	0.166	0.183	0.177	0.199	0.209	–	0.216	–	0.228
Residual alkali, g/l	13.8	13.2	12.6	–	12.4	–	12.1	–	11.6
Stabilisation with BH									
Yield loss	0.090	0.094	0.105	0.116	–	–	0.137	–	0.144
Residual alkali, g/l	15.0	14.8	–	14.3	–	–	13.6	–	13.3
Stabilisation with AQS									
Yield loss	0.059	0.088	0.095	0.094	0.133	–	0.139	–	0.164
Residual alkali, g/l	14.8	13.1	13.4	12.7	12.5	–	12.4	–	12.1

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