



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.

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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, & Krottschek, 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, Hrutford, & 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, anthraquinone-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:

$$\left\{ \begin{array}{l} \frac{dR}{dt} = -k_s R, \end{array} \right. \quad (1)$$

$$\left\{ \begin{array}{l} \frac{dP}{dt} = k_p R, \end{array} \right. \quad (2)$$

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 $*-2pt$

$$R = R_0 e^{-k_s t}. \quad (3)$$

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

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

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

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

The kinetics of alkaline hydrolysis was studied by Lai and Sarkanen (1967). Later, Van Loon and Glaus (1997) and Pavašars,

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).

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

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)_{opt}). The BH half-life in aqueous conditions dependent on the pH and the temperature of the reaction was calculated as

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

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_{opt}), AQS (OA CL-AQS_{opt}), and BH (OA CL-BH_{opt}), where opt denotes the optimisation of stabilisation agent concentrations.

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