

COMPREHENSIVE KINETIC STUDY OF DELIGNIFICATION, CARBOHYDRATE DEGRADATION, CELLULOSE CHAIN SCISSIONS AND HEXENURONIC ACID REACTIONS DURING KRAFT PULPING PROSOPIS CHINENSIS

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ABSTRACT: Prosopis Chinensis represents one of the most suited fiber sources for the production of a wide range of high quality papers and high-purity dissolving pulps. The optimization of kraft pulping covering both continuous and batch processes demands kinetic models suitable for advanced control and offline optimization of the cooking operation.

Quite recently, an improved kinetic model structure for softwood kraft cooking has been published, which considers varying alkali and temperature profiles during the cooking [1]. Unfortunately, most alkaline cooking models are based solely on softwood [2, 3]. This work contributes to an improved kinetic model for kraft cooking of Prosopis, suitable for advanced control of modern displacement cooking processes such as the continuous batch cooking process (CBC). After impregnation where the initial lignin has been removed, the bulk and residual delignification have been studied in a batch reactor as a function of the [OH-], [HS-], ionic strength, [Na+], and temperature. The underlying kinetic expressions are similar to those used in the Andersson model also including a mechanism for determining kraft pulping of Prosopis chinensis, the distribution of lignin and carbohydrate species 2 and 3 as a function of the cooking conditions. The kinetic equations were successfully validated against experimental data from a pilot plant digester applying conventional batch cooks.

Furthermore, the formation of hexenuronic acid bound to the xylan backbone and its degradation / dissolution were described by a consecutive first-order reaction. In agreement to other studies, the temperature and the effective alkali charge revealed a strong influence on the hexenuronic acid content in the pulp while the effect of sulfidity proved to be insignificant. The role of ionic strength on the HexA content remained unclear. An increase in the ionic strength resulted in a higher maximum HexA content shifted to a higher kappa number (about 58), but with progressive delignification to a kappa number typical for unbleached Prosopis Chinensis, kraft pulp (about 15), the HexA content decreased to a level more than 20% lower as compared to pulps cooked at lower ionic strength.

Keywords: Prosopis cheinesis, kinetics & CBC pulping

INTRODUCTION

The majority of kinetic studies have been performed with softwoods. So far, only basic information about the kinetics residual phase and also modeled the lignin conversion value at the transition point from the bulk to the residual phase. However, none of the presented models was able to meet all necessary requirements for modeling *Prosopis* CBC kraft pulping. *Prosopis Chinensis* belong to the family Leguminosae Mimosaceae. It is an unarmed tree or shrubs with drooping branches, found either in a wild or cultivated state in the drier parts of India.

CBC is a new pulping method, which allows changing the alkali profile and other important reaction conditions during the cooking process [6]. The model of choice seems to be the model proposed by Andersson et al. [1]. This model considers the influence of varying cooking conditions by introducing an appropriate algorithm for determining the distribution of lignin and carbohydrate

species 2 and 3 as a function of the relevant cooking conditions. The aim of this study was to develop a comprehensive kinetic model for kraft pulping of *E. globulus* based on the concept of Andersson to provide an appropriate tool for the optimization of cooking processes in practice.

Characteristic for hardwood kraft pulps is their relatively high content of hexenuronic acid groups (HexA) linked to the xylan backbone. Different to softwood pulping, in hardwood pulping the decrease in HexA content seems to occur only at very low kappa numbers, normally not achieved during commercial pulping processes [7]. The presence of HexA in hardwood kraft pulps contributes to 25 - 30% of the pulp kappa number and thus explains the low efficiency of oxygen delignification of hardwood kraft pulps. Recently, some efforts have been made to better understand the mechanisms of both the HexA formation and HexA degradation/ dissolution [7-11]. So far, it is agreed that the HexA reactions are mainly dependent on temperature and alkali charge, which concludes that a considerable decrease in HexA contents can only be achieved when high temperatures and high alkali charges are applied.

The present work proposes a simplified kinetic model that describes the formation of HexA from 4-O-methyl- α -D-glucuronic acid (MeGlcA) and the degradation/ dissolution of HexA during kraft pulping of *Prosopis Chinensis*. Moreover, the influence of effective alkali concentration, the sulfidity of the cooking liquor and the ionic strength, expressed as sodium ion concentration, on the HexA concentration profiles are exemplified.

EXPERIMENTAL

For the kinetic studies the sample of *Prosopis Chinensis* were collected from different places of Vidisha & Raisen district of Madhya Pradesh. The part of *Prosopis Chinensis* plant i.e., wood were collected in the month of July- August 2009. The wood of *Prosopis Chinensis* with an average thickness of 4 mm were further cut in the laboratory. After screening their average dimensions were reduced to 9.6 mm in length, 4.9 mm in width and 1.9 mm in thickness. The wood chemical composition was as follows: 22.1 % Klason lignin (KL) (T 222 om-98), 4.6 % acid soluble lignin (T om- 250), 47.3 % cellulose (C), 2.2 % glucomannan (GM), 21.8 % 4-O methyl glucurono xylan (X) (AEC with PAD detection after total hydrolysis with H₂SO₄) and 2.0% resins and ash (T 211 om-93; ISO 14453:1997). The hexenuronic acid (HexA) content in the pulp was determined by a selective hydrolysis of the glycosidic linkage between the hexenuronic acid group and the xylan chain followed by oxidation and conversion to a coloured compound for colorimetric determination [12]. The kappa number <20 was determined according to T236 cm-85, and >20 according to SCANC 1:00, the viscosity according to SCAN 15:88. The cooking liquors were prepared from NaOH(s), Na₂S.H₂O(s), and NaHS(s). The sodium concentration was adjusted by gravimetric addition of NaCl. Effective and residual alkali concentrations were analyzed according to SCAN-N 30:85 and sulfidity according to SCAN-N 31:94.

Prior to the kinetic investigations, the wood was subjected to a uniform impregnation stage in a 10 L-digester at 100 °C for 60 min with [OH⁻] = 0.37 mol/L, [HS⁻] = 0.16 mol/L, [Na⁺] = 1.5 mol/L at a L/S ratio of 10:1. With a yield loss of 6.5%, the composition of the impregnated wood changed to 18.9 % KL, 47.1 % C, 0.7 % GM, 17.9 % X, and 1.5 % resins and ash. KL can be calculated from kappa number by a factor of 0.183 (18.9/103.3).

After drainage of the impregnation liquor, the chips were transferred to a 400 ml-Parr reactor to proceed with the kinetic investigations. The stainless steel pressure vessel was provided with an external heating system and measurement and control of both pressure and temperature. The temperature was increased at a rate of about 5 °C per minute to the preset cooking temperature. The heating-up time and any deviation from the target cooking temperature were corrected for isothermal conditions using the following expression: 1

$$\int_{t_{T0}}^{t_{T1}} \left[\text{Exp} \left(-\frac{Ea}{R} \left[\frac{1}{Tt} - \frac{1}{TTo} \right] \right) \right] dt \quad (1)$$

in which Tt is the temperature during heating-up, T0 the target temperature, tT0 the reaction time at target temperature (corrected for isothermal conditions), and EA the activation energy which was assumed to be 134 kJ/mol. The numerical integration can be carried out by just adding the terms as follows using an Excel sheet (Eq. 2).

$$t_{T0,n} = t_{T0,n-1} + (t_{Tt,n} - t_{Tt,n-1}) \left(\text{Exp} \left(\frac{EA}{R} \left[\frac{1}{Tt,n} - \frac{1}{T0} \right] \right) + \left(\text{Exp} \left(-\frac{EA}{R} \left[\frac{1}{Tt,n-1} - \frac{1}{T0} \right] \right) \right) / 2 \right) \quad (2)$$

The experiments were accomplished at an L/S ratio of 40:1 in order to keep constant concentration of chemicals throughout the cooks. Time series at four different temperature levels (140, 150, 160, and 170°C), five different [OH⁻] levels (0.1, 0.27, 0.52, 0.94 and 1.23 mol/L), three different [HS⁻] levels (0.17, 0.29, 0.64 mol/L) and three different [Na⁺] levels (0.8, 1.5 and 2.5 mol/L) were conducted to provide the necessary database for the evaluation of the kinetic models for delignification, carbohydrate degradation and cellulose chain scissions. For the kinetic investigations of both, HexA formation and HexA degradation/ dissolution, the conditions given in Table 1 were applied

Table 1: Cooking conditions of Prosopis Chinensis kraft cooking used for the kinetic investigation of HexA formation and HexA degradation

Parameter	Units	Changed Parameters				Const. Parameter
Temperature	°C	140	150	160	170	160
[OH ⁻]	mol/L	0.10	0.52	1.23		0.52
[HS ⁻]	mol/L	0.17	0.28	0.64		0.28
[Na ⁺]	mol/L	0.80	1.5	2.50		1.50

RESULTS AND DISCUSSION

Kinetics of delignification and carbohydrate degradation.

The general structure of the delignification and carbohydrate degradation models is derived from the model introduced by Andersson et al. ^[1]. The advantage of this model is that it accounts for any subsequent changes in cooking conditions as occurring in industrial batch and continuous cooking processes (see also ^[13]). It is commonly agreed that the single wood species such as lignin (L) and (CH) can be divided into three species with different reactivity (L1, L2, L3 and CH1, CH2, CH3) representing their different chemical and supra molecular composition.

The model is based on the assumption that all species react in parallel throughout the cook. Assuming that a great part of species 1 (L1, CH1) is easily degraded during impregnation it is suggested to consider only species 2 and 3 (L2, L3, CH2, CH3) for both delignification and carbohydrate degradation models. In the case of non isothermal industrial cooks, the initial chemical wood composition (L0, CH0) has to be used as starting values to account for the overall consumption of active cooking chemicals ([OH⁻], [HS⁻]).

A general rate equation for both lignin and carbohydrate degradation can be expressed according to Eq. 3.

$$\frac{dW_{i,j}}{dt} = -k_{Wi,j} W_{i,j} \quad (3)$$

for $W_i = L$ for lignin and CH for the sum of carbohydrates comprising cellulose (C), glucuronoxylan (X) and glucomannan (GM), for $j =$ species 2 and 3 for both L and CH and for $k =$ rate constants. The general solution for these first-order rate equations is given in Eq. 4

$$W_{i,tot} = \sum_{j=2}^3 W_{i,j} \text{Exp}(-K_{Wi,j}t) \quad (4)$$

for $W_{0i} = L$ and CH concentrations after impregnation for the evaluation of the kinetic models and initial wood composition for modelling of industrial cooks.

The dependency of the rate expressions, $k_{Wi,j}$, on the reaction conditions can be described according to Eq. 5:

$$K_{Wi,j} = A_{Wi,j} \text{Exp} \left[\frac{EA_{Wi,j}}{R} \left(\frac{1}{443} - \frac{1}{T} \right) \right] \cdot ([OH^-]^a [HS^-]^b [Na^+]^c + Kr) \quad (5)$$

for $A =$ pre-exponential factor, $EA =$ activation energy [kJ/mol], $R =$ gas constant [kJ/(mol.K)], $a, b, c,$ are constants and kr a rate constant reflecting the observation of carbohydrate degradation even at very low alkali concentrations. The experimental results have been fitted by nonlinear regression using Scientist® as data fitting software. Scientist employs a least squares minimization procedure based on a modification of Powell's algorithm. The fitting yields the results shown in Table 2.

Please note, that similar to Andersson et al., the pre-exponential factors A were modified by a “factor” reflecting the (not considered) differences between constant composition cooks and industrial pulping. Table 2 shows that the activation energies are in the range reported for kraft pulping, except in the case of carbohydrate degradation of species 3, whose activation energy is significantly higher as published for the same reaction in spruce (174.6 kJ/mol compared to 144 kJ/mol reported by Andersson et al. ^[1]). Moreover, the kinetic order of the hydroxide ion concentrations, particularly for L3 and CH3, are far higher as reported in the literature ^[13]. The large order for [OH⁻] in the case of L3 may be attributed to its simultaneously high dependency on [Na⁺]. The results from the kinetic study confirm that an increase in the ionic strength shown in table 2.

Table 2: Kinetic constants for delignification and carbohydrate degradation Prosopis Chinensis

Component	L0 odw	CH0 kappa #	A % odw	EA	1/ (M*m in)	a kJ/mo l	b kJ/mo l	c kJ/mo l	kr 1/min
Lignin including HexA									
L1*	3.2	-	-	-	-	-	-	-	-
L	17.	93.5	0.452	131.4	0.63	0.32	0.63	1.3	0.00
L3	1.8	9.0	0.0402	133.0	1.47	0.00	0.68	0.5	0.00
CH1*	-	5.6							
CH2	-	15.3	0.2415	140.9	1.54	0.00	0.00	1.0	0.11
CH3	-	0.3	0.0031	174.6	2.35	0.00	0.00	2.0	0.00

*calculated from mass balance

Decreases the rate of delignification considerably as shown for birch by Lindgren and Lindström ^[14] and Changes in ionic strength, however, exhibit no significant influence on carbohydrate degradation. To allow for changes in the main reaction conditions such as [OH⁻], [HS⁻], [Na⁺] and temperature, the distribution model proposed by Andersson et al. ^[1] has been implemented in our cooking model. This model shows that the species W2 and W3 interchange reversibly and that the equilibrium between both species is dependent on certain reaction conditions. The intersection is the level of wood component where W2 equals W3 and is termed W*. Multiple regression analysis provides an expression for W* as a function of the reaction conditions. The expressions for L* and CH* are given in Eq. 6 and 7, respectively, in which the temperature T is expressed in °C. The dependency of the extracted intersections L* on the [OH⁻], [Na⁺] and [HS⁻].

Surprisingly, no clear influence of L* on temperature has been observed, while CH* was clearly influenced by temperature and [OH⁻] but not by [HS⁻] and [Na⁺].

The way of determining the proportions of W2 and W3 follows the procedure given by Andersson et al. ^[1, 13].

Kinetics of cellulose chain scissions

The kinetics of carbohydrate degradation, observed as viscosity loss or cellulose chain scissions, can be followed by a very simple approach with reasonable precision. Equation 8 describes the cellulose chain scissions as a function of temperature, effective alkali and sodium ion concentrations and time.

$$L^*=0.001487([\text{OH}^-]+0.025)-0.625([\text{HS}^-]+0.045)-0.308([\text{Na}^+]+5.0) \quad (6)$$

$$\text{CH}^*=55.44+68.45.[\text{OH}^-]-0.48-T.[\text{OH}^-] \quad (7)$$

$$\left(\frac{1}{\text{DPn},t} - \frac{1}{\text{DPn},o}\right) = A \text{Exp}\left(\frac{EAc}{R T}\right) [\text{OH}^-]^d [\text{Na}^+]^e t \quad (8)$$

$$D=0.057\sqrt{T} \text{Exp}\left(-\frac{2452.4}{T}\right) (0.00364.k\#+0.13[\text{OH}^-]0.55+0.58) \quad (9)$$

Using this simple expression, it is permissible to use DP_v , calculated from intrinsic viscosity according to SCANCM- 15:88, instead of DP_n . Nonlinear regression using least square minimization procedure yields the coefficients for the applied kinetic model shown in Table 3:

Table 3. Kinetic constants for chain scissions during kraft pulping of *Prosopis Chinensis*

Model Parameter	Units	
DP_{no}		4900
$\ln A$	1/(M*min)	36.48
EAc	kJ/mol	180.3
d		1.08
e		0.74

Unlike to carbohydrate degradation, an increase in ionic strength at a given $[\text{OH}^-]$ is connected with an increase in cellulose degradation. It may be speculated that the presence of high $[\text{Na}^+]$ promotes chain cleavage due to a better accessibility of the glycosidic linkages.

Effective concentration of cooking chemicals

Chip dimensions and the level of cooking chemical concentrations in the bulk liquor influence the concentration profiles of the cooking chemicals within the wood. The $[\text{OH}^-]$, $[\text{HS}^-]$ and $[\text{Na}^+]$ across the chip thickness (one-dimensional chip model) were calculated by using the diffusivity parameters of McKibbins solving Fick's second law of diffusion corrected with respect to pH and lignin content [15, 16], where D is the diffusion coefficient in $\text{cm}^2\text{min}^{-1}$ and T the temperature in K.

The reactive cooking chemicals, $[\text{OH}^-]$ and $[\text{HS}^-]$, are transported from the bulk phase to the boundary layer and finally through the water layer of the cell wall and pit membrane structure under the influence of their concentration gradient in the entrapped and free liquor.

The model considers only the diffusion of alkali in a one-dimensional wood chip through the chip thickness (radial direction). The diffusion of $[\text{OH}^-]$ is described by Fick's second law of diffusion. The concentration of the active cooking chemicals in the entrapped liquor (bound liquor) must be determined to provide the necessary data for a reliable kinetic study which may be used to predict the course of pulping reactions in pilot or even commercial digesters.

At the beginning of the cook, at $t = t_0$, the average $[\text{OH}^-]$ in the entrapped liquor depends on the wood density (ρ_{dc}) and the moisture content (MCW) of the wood according to Eq. 10:

$$[\text{OH}^-]_{\text{EL}} = \left[1 - \frac{MCW}{(100 - MCW) \cdot \left(\frac{1}{\rho DC} - \frac{1}{1.53} \right)} \right] [\text{OH}^-]_{\text{FL}} \quad (10)$$

Where FL is the free or bulk liquor, EL the entrapped or bound liquor.

During pilot plant or industrial cooking, where L/S ratios range between 2.5 and 5, the concentration of cooking chemicals decreases as a result of the consumption of chemicals by the reaction products. Thus consumption of active cooking chemicals must be considered to predict the extent of delignification and carbohydrate degradation accurately. The specific consumptions of [OH⁻] were determined as 0.20 NaOH/kg degraded lignin and 0.45 kg NaOH/kg degraded carbohydrates, respectively, which are only slightly higher as reported by Christensen et al. for similar reactions of softwood components¹⁷.

The concentration profiles for the effective alkali in both free (FL) and entrapped (EL) liquors (average concentration) during a conventional batch kraft cook using *Prosopis Chinensis* as a raw material have been calculated by the model. Additionally, the minimum EA concentration is in the center of the 4 mm chip (CC). The EA concentration in the bound liquor reveals an increase during the first third of the heating-up phase, approaching the maximum value after 33 min at 115 °C, indicating that diffusion is the dominating process. The effective alkali, however, is rapidly consumed by the chemical reactions which start heavily in the second third of the heating-up period. The EA concentration inside the chips approaches that outside the chips only after 30 min reaction time at cooking temperature.

The calculated residual EA concentration (after $t = 90 + 112 = 202$ min) of 0.300 mol/L agrees perfectly with the experimentally determined residual EA concentration of 0.296 mol/L.

Validation of the Model

One of the key advantages of the distribution model from Andersson is that it accounts for changes in the reaction conditions appropriately.

Therefore, in a first set of experiments the influence of a sudden increase of [OH⁻] from 0.1 mol/L to 1.0 mol/L after a reaction time of 45 min at 160 °C and an L/S ratio of 40:1 on the course of the degradation of wood components was simulated. Figure 4 displays the comparison between predicted and experimentally determined kappa numbers. Even though only a few experiments were carried out so far, the correspondence between calculated and measured kappa numbers is satisfactory. The (calculated) course of [OH⁻] in both the bound liquor and the chip centre is quite comparable due to the high L/S ratio. The aim of the second set of experiments was the prediction of the unbleached pulp quality derived from *Prosopis Chinensis* kraft pulping using a conventional batch process.

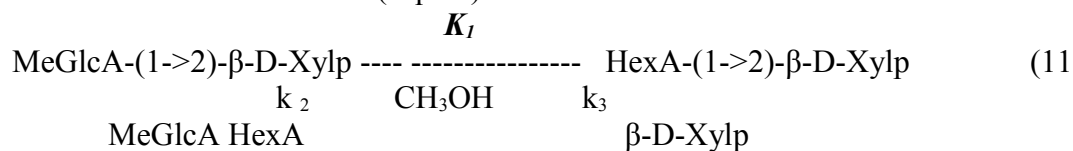
The mean thickness of the industrial chips was 4.0 ± 1.5 mm and the chips had a moisture content of 35%. The cooking trials were carried out in a 10-L digester with forced liquor circulation. After a short steaming phase (8 min, final temperature 98 °C), white liquor was introduced to a total L/W ratio of 2.96 L/kg. The effective alkali charge was set to 19% on od wood. The sulfidity was 26.5% resulting in initial [OH⁻] and [HS⁻] of 1.60 mol/L and 0.245 mol/L, respectively. The conventional batch cooking procedure was characterized by a heating-up time of 90 min to a cooking temperature of 160 °C. Four cooks were performed comprising H factors of 300, 450, 600, and 800.

Figure 5 illustrates an acceptable correspondence between simulated and experimentally determined kappa numbers and viscosity values. Even though the modeling of viscosity is based on a very simple approach, the viscosity is predicted more precisely as compared to the kappa number. The latter reduces only by 3.5 units when increasing the H-factor from 300 to 800. The low change in kappa number during a significant prolongation of cooking time may be attributed to a progressive precipitation of dissolved lignin.

Formation and degradation /dissolution of hexenuronic acid (HexA) in pulp during kraft pulping

Hexenuronic acid (4-deoxyhex-4-enuronic acid or HexA) is formed from 4-O-methyl- α -D-glucuronic acid (MeGlcA) after β - elimination of methanol during the preliminary cooking stages. HexA contributes to the kappa number (11.6 mmol of HexA corresponds to 1 kappa unit)^[18] and causes an increased brightness reversion of pulp and paper^[19]. The HexA concentration profiles in softwood differ significantly from those reported in hardwood pulping^[7]. The formation of HexA in softwood pulping is very fast, and their degradation/dissolution of HexA starts already in the bulk phase of the cook^[20]. Gustavsson et al. investigated the influence of hydroxyl ion [OH⁻] concentration, hydrogen sulphide ion [HS⁻] concentration, ionic strength [Na⁺] and temperature, on the degradation/dissolution of HexA in kraft pulping of spruce^[21]. According to a simplified kinetic model, the rate of HexA removal increases with increasing [OH⁻], increasing [Na⁺], increasing [HS⁻], and increasing cooking temperature. Taking the delignification kinetics into account, this translates into a reduced HexA content at a given corrected kappa number (the kappa number of HexA is subtracted) by applying a high [OH⁻], a high [Na⁺], a low temperature, and a low [HS⁻]. It is widely agreed that the HexA content of hardwood pulps increases during the initial phases of bulk delignification and does not decrease until very low kappa numbers are attained [7]. Because the pulp will not cook to such low kappa number in mill practice, HexA content of hardwood pulps is significantly higher as compared to softwood pulps. Both the lower HexA formation and the delayed HexA reduction rates in conventional kraft pulping of hardwood as compared to softwood has been attributed to the higher EA consumption in the early stages of cooking due to a higher demand for neutralization of the formed hydroxycarboxylic acids originated from the degradation of hemicelluloses. This clearly indicates that hydroxide ion concentration and the temperature level are decisive parameters controlling the HexA concentration both in the pulp and in solution.

The decrease of MeGlcA in pulp through HexA formation or the cleavage of methylglucuronic acid and subsequently the cleavage of HexA from the xylan backbone can be described by consecutive reaction kinetics (Eq. 11):



The energies of activations for HexA formation (116.5 kJ/mol) and HexA degradation/dissolution (140.3 kJ/mol) listed in Table 4 are quite comparable to those reported by Danielsson et al. although, differently to our investigations, they considered the HexA content of the sum of the pulp xylan and the dissolved xylan. In contrast, the corresponding activation energies for HexA formation and HexA degradation reported by Simao et al. ^{18, 91} were at a significantly low level (92 and 110 kJ/mol, respectively) also compared to the activation energies for degradation of carbohydrates and delignification (see Table 2 and [1]) indicating that, with increasing temperature, the HexA side groups will be progressively degraded while the carbohydrate and lignin contents in the pulp remain less affected. However, the results are not comparable because their approach with respect to experimental conditions and the proposed reaction scheme was somewhat different.

Following the HexA content of the pulp as a function of the kappa number it can be seen that the HexA degradation/dissolution exceeds the HexA formation only at kappa numbers below 15 (on pulp), even though the [OH⁻] is kept constant at 0.52 mol/L. The agreement with result of the kinetic investigation (table 2&4) the HexA content in pulp xylan at a given kappa number decreases with increasing temperature.

It is widely accepted that the level of hydroxyl ion concentration controls both the formation of HexA by the elimination of the 4-*O*-methoxyl group and the degradation/dissolution of HexA by alkaline cleavage of HexA from the xylan backbone or by dissolution of HexA linked to the xylan chain. In their kinetic study Simao et al. reported rather high reaction orders on the hydroxyl ion concentration. The order for degradation/dissolution being higher than for HexA formation indicating a lowering of the HexA content in the pulp xylan when increasing the effective alkali concentration during residual delignification ¹⁸¹. The strong influence of [OH⁻] on the HexA concentration profiles has been confirmed in our study.

Interestingly, the HexA content in pulp continues to rise for kappa numbers below 15 at an effective alkali concentration of only 0.10 mol/L as demonstrated. This may be explained by the observation that at a low hydroxyl ion concentration re-precipitation of HexA Xylan fractions dominates over alkali induced splitting of the HexA side chain.

Unfortunately, the highest HexA content in the unbleached pulp, kappa number 12 to 20, occurs at a medium [OH⁻] of 0.52 mol/L, typical for modern displacement cooks. Obviously, this level of effective alkali concentration is not yet sufficient to favour the cleavage of the HexA side chain. It needs more than twice the [OH⁻] to keep the HexA content at a low level (around 10 mmol/kg wood). However, such conditions are known to decrease pulp yield, particularly the hemicelluloses content and thus deteriorate pulp strength. In agreement with other authors, the sulfidity of the cooking liquor displays not a noticeable influence on the HexA concentration profiles ^{19, 231}.

However, when plotting the HexA content in pulp against the kappa number, the sulfidity appears to affect the HexA content. The effect of sulfidity may be attributed to its accelerating influence on the delignification rate rather than on a direct involvement in the HexA reactions.

An increase in ionic strength from 1.5 mol/L to 2.5 mol/L leads to a dramatic increase of the maximum HexA content in the pulp at a kappa number of about 35 on dry wood (corresponding to a kappa number of about 58 on dry pulp) as depicted. The shift of the maximum HexA content to considerably higher kappa numbers can be attributed to the negative impact of a high ionic strength on the delignification rate (Table 2).

The small figure inside Figure 10 reveals that the maximum HexA content in pulp appears after the same reaction time while the level is almost 40% higher as compared to the HexA content at lower levels of ionic strengths, 1.5 mol/L and 0.8 mol/L, respectively. A closer examination shows that both reaction rates increase with increasing ionic strength. An increase in ionic strength, expressed as [Na⁺], was found to promote the rate of HexA degradation also in kraft pulping of Norwegian spruce ¹²¹. It may be speculated that the HexA formation reaction (k₁) is favored over the cleavage reaction of MeGlcA from the xylan backbone with increasing [Na⁺].

Adequate model experiments have been undertaken to elucidate the reason for the increase of both HexA formation and degradation rates along with an increase in ionic strength

CONCLUSION

The proposed kinetic model adequately describes the performance of lignin and carbohydrate degradation and cellulose chain scissions during kraft pulping of *Prosopis Chinensis*. For the first time also the influence of $[Na^+]$ was considered in a comprehensive kinetic pulping model. The good correspondence between predicted and experimentally determined unbleached pulp parameters confirms the suitability of the distribution model introduced by Andersson et al. for offline optimization studies of industrial kraft cooks.

Furthermore, the formation of HexA bound to the xylan backbone and its degradation/dissolution were described by a consecutive first-order reaction. Unfortunately, the results were not very encouraging and confirmed the results of other authors in broad terms in a sense that the HexA content cannot be reduced to low levels by choosing appropriate cooking conditions without simultaneously deteriorating pulp quality and decreasing pulp yield. The energies of activation for the formation of HexA, the degradation/dissolution of HexA, and the delignification of *Prosopis Chinensis* during kraft pulping were found to be 116.5, 140.3, and 131.4 (L2) or 133.0 kJ/mol (L3), respectively. The differences in activation energies indicate that cooking at higher temperature may be advantageous to achieve a lower HexA content in the pulp. A very high alkali concentration, especially in the later parts of the cook, is necessary to substantially decrease the HexA content. Such cooking conditions, however, are known to degrade the carbohydrates, particularly the hemicelluloses, and consequently to decrease pulp yield and pulp strength. The role of ionic strength, expressed as $[Na^+]$, on the HexA content is not yet elucidated. An increase in the ionic strength resulted in a higher maximum HexA content shifted to a higher kappa number (about 58), but with progressive delignification to a kappa number typical for unbleached *prosopis cheinesis* kraft pulp (about 15), the HexA content decreased to a level more than 20% lower as compared to pulps cooked at lower ionic strength.

However, more work has to be conducted to create an understanding of the reactions of the single wood components including the different hemi cellulose substances, molecular and supra molecular structure of cellulose and alien substances such as resins and inorganic components.

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