An improved kinetic model structure for softwood kraft cooking

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Summary

The recent rapid development of cooking strategies for continuous kraft digesters suggests that optimal operation is still elusive. This work exposes, in light of modern experimental findings, flaws in the commonly employed kinetic models for kraft delignification. An improved kinetic model is proposed to better account for the observed phenomena in recent experiments, and is expanded to include expressions for the kinetics of hemicellulose components which are important parameters that influence the final quality and yield of the product pulp. The models were developed using data obtained from the literature and were validated against experimental data obtained from an instrumented laboratory circulation digester and a laboratory autoclave.

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The economic operation of a continuous digester practically demands model-based optimisation and control. The kernel of such a model is the description of the kinetics of the chemical reactions that occur in the digester. If these expressions are faulty, then any subsequent optimisation will be of no value. The current trend to deliver pulps tailored to a customer's particular needs means that no single operation, perhaps established by trial and error or heuristics, is likely to be optimum across the entire production portfolio. The challenge to optimise production places considerable demands on the modelling requirement, notably in regions that have been previously partially overlooked.

The contribution of this work is an improved kinetic model for kraft cooking suitable for advanced control and offline optimisation of the cooking operation. The models are validated against experimental data from an instrumented laboratory circulation digester and a laboratory autoclave. The eventual aim is to use this model that describes the complex chemical kinetics in the vessel in order to drive it in a near optimum manner to ensure the economic success of the production. Given the high running costs of industrial-scale digesters, difficulties in sampling, and the large time delays, laboratory cooking studies and modern modeling tools are the most efficient ways to develop near-optimum cooking schemes (Andersson et al. 2002b; Sandström 2000). Such kinetic models can still be incorporated in model-based controllers such as described by Bhartiya and Doyle III (2002) or Michelsen et al. (1994) in order to improve the regulatory response and consequently improve the overall economics.
Experimental

Experimental data is required to quantitatively assess the performance of previously published models, expose any possible deficiencies, and to validate new models. This data was obtained both from the literature, primarily the extensive series of experiments documented in Lindgren and Lindström (1996) and Lindgren (1997), and from circulation and autoclave digesters experiments performed in this study as described in Andersson et al. (2001). Cooking times for these later experiments using laboratory screened industrial spruce chips (*Picea Abies*) ranged from 15 to 315 minutes with cooking temperatures between 150–167°C, and effective alkali charges between 10–25% on wood, using both conventional and modified schemes. The ranges imply that some cooks were interrupted even during the heating up or impregnation stage.

For the autoclave cooks, the pulps were analysed for determination of pulp yield, kappa number, and chemical composition (lignin and carbohydrates). The lignin content was determined as Klasson lignin (acid insoluble lignin according to the Tappi method T 222 cm-83) and the content of carbohydrates (glucose, mannose, xylose, arabinose and galactose) was determined using ion chromatography ( Dionex PA-1 column and electrochemical detection), after the pre-hydrolysis stage in the Klasson lignin analysis. Subsequently the content of cellulose, (galacto-) glucomannan and (arabino-) xylan content was calculated, assuming a mannose-glucose ratio of 3.5 in the glucomannan, using Eqns. 1-3. The liquors were analysed for concentrations of hydroxide ion, [OH\textsuperscript{-}], (SCAN-N 33:94) and hydrogen sulfide ion, [HS\textsuperscript{-}], (SCAN-N 31:94) and organic matter content (Andersson et al. 2001). Both bound and free liquor from the autoclave cooks were analysed using the techniques developed by Andersson et al. (2001).

In the case of the circulation cooks, an inline NIR analyser was used to extract 14 key cooking liquor parameters as described by Andersson and Wilson (2002). The origin of the dissolved organic matter was determined using NIR analysis of the cooking liquor. From the data obtained the pulp yield and composition were calculated indirectly via a mass balance.

Nomenclature

In the subsequent model development, the following nomenclature is employed. Wood is characterised by the four components: lignin (L), cellulose (C), glucomannan (G), and xylan (X). Within each of these four components, three species are used to capture the diversity in reactivity and dissolution patterns. This gives a total of twelve states, namely \( L_1, L_2, L_3 \) for lignin, \( C_1, C_2, C_3 \) for cellulose and so on. The total carbohydrates (C, G, and X together) are denoted \( CH \). It is assumed that all states exist and react in parallel at any one instance in time. Consequently, the cook is not divided into consecutive ‘stages’ as has been proposed in earlier studies such as Gustafson et al. (1983), nor is the term phase employed (as in ‘residual phase lignin’) in order to describe the state of aggregation.

\[
C = \text{glucose - mannose} \cdot \frac{1}{3.5} \quad (1)
\]
\[
G = \text{mannose} \cdot \left(1 + \frac{1}{3.5}\right) + \text{galactose} \quad (2)
\]
\[
X = \text{xylan} + \text{arabinose} \quad (3)
\]

Existing kraft cooking kinetic models

Two broad main families of digester kinetic models appropriate for optimisation and control are chosen as representative. They are the ‘Purdue’ family, derived at Purdue University, USA, and the ‘Gustafson’ family, derived at University of Washington, USA, although both families can be traced to the pioneering work of LéMon and Teder (1973). Comparisons presented by Andersson et al. (2002a,b) illustrate that the models
exhibit significant differences, both regarding structure and response to process changes, thereby consequently indicating different optimal operating conditions. Some investigations (Harkonen 1987; Johnsson 1971; Michelsen 1995) are more concerned with the physical flows within the digester, or how the packing degree affects the operation as opposed to the reaction kinetics. These complicated flow models often use only simplified kinetics.

The Purdue model

One of the earliest complete models for kraft cooking kinetics known as the Purdue model was developed by Smith (1974). The Purdue model assumes that five wood states are sufficient to describe the digester internals, namely high- and low-reactive lignin, and carbohydrate components $C$, $G$, $X$. These five states are augmented with the liquor states, [OH$^-$] and [HS]. Christensen et al (1983) and Saltin (1992) subsequently improved the model by introducing un-reactive components increasing the flexibility of the rate expression to

$$\frac{dW_i}{dt} = \left(k_{i1}[\text{OH}^-] + k_{i2}[\text{HS}^-]\right)(W_i - W_i^\infty)$$  \hspace{1cm} (4)

where $W_i$ are the five wood components, and $W_i^\infty$ denotes the un-reactive components. Full continuous digester models using these kinetic expressions have been developed (Bhartiya and Doyle III 2002; Christensen et al 1983; Kayihan 2002; Saltin 1992; Wisnewski et al. 1997).

The Purdue model, (Eqn. 4), and close variants, have long been considered the default kinetic model for dynamic studies of industrial digesters. However, in recent developments Lindgren and Lindström (1996) plot the log lignin concentration against time showing a transition in gradient part-way through the cook. This phenomenon is explained following a proposal by Teder and Olm (1981) by introducing an extra lignin species where the initial concentrations are found to be dependent on the dosing of alkali. Despite the fact that this model describes only lignin, we consider it to be a development of the Purdue model since it uses the concept of parallel reactions.

In summary, the Purdue family of models uses five wood components reacting in parallel, with possible un-reactive portions. The same structure for the rate expressions is used throughout the cook. In all, 36 parameters are needed to characterise the kinetics.

The 3-stage model

Gustafson et al. (1983) developed a slightly different form for the kinetics. Rather than use five wood species states as in the Purdue case, the wood components are divided into only two: lignin, and carbohydrates. However, the kinetics are more complicated as the reactions are divided into three consecutive stages termed in the original work, initial, bulk and residual with different kinetic expressions in each. The majority of the delignification occurs following a rate expression similar to Eqn. 4, while the carbohydrate degradation is always a ratio of the lignin degradation. If the carbohydrate yield is plotted as a function of lignin, (e.g. Olm and Tistad (1979), as seen in Fig. 1 where our data have also been superimposed, three distinct stages show as piecewise linear lines.

An extension to model modified cooking schemes developed by Pu et al. (1991) separates the carbohydrates into cellulose and hemicellulose and assumes [HS$^-$] is not consumed. Two recent studies which use a simplification of the diffusion model in Gustafson et al. (1983) are Meghanathan et al. (1999) and Vanchinathan and Krishnagopalan (1997) which complement the development by using online measured data.

To summarise, the 3-stage family models use two or three wood components, that react in three consecutive stages, according to different kinetics in each stage. Some of the latter models in this family include un-reactive portions in a manner similar to Purdue model kinetics in Eqn. 4. In total, the model originally
proposed by Gustafson et al. (1983) uses 17 parameters, while the subsequent revisions use from 13 to 32 parameters.

Fig. 1. The carbohydrate yield as a function of delignification showing three distinct stages as described by Gustafson et al. (1983). Superimposed are autoclave cook data, □, from the present study.

### An improved model for kraft cooking kinetics

Due to the importance of the lignin degradation reactions, they have been the topic of intensive study for some decades. However, recent experimental observations expose the limitations of the established models reviewed above. In Fig. 2 the Purdue model of Christensen et al. (1983) and the 3-stage model of Gustafson et al. (1983) are overlaid the experimental data from Lindgren and Lindström (1996) for different [OH] levels and [OH] step changes. Clearly neither model successfully follows the data, particularly when the alkali conditions are varied. Due to the structural problems evident in both models, simply re-fitting the model parameters does not significantly improve the model performance.

The existence of unreactive lignin as introduced by Saltin (1992) for the Purdue family or Pu et al. (1991) for the 3-stage family is questionable (refer Fig. 2) as pointed out by Andersson et al. (2002b) and Lindgren and Lindström (1996). In addition, from the shape of the lignin degradation curve, one can see that at least two species are required to describe the data. From Kondo and Sarkanen (1983) and Olm and Tistad (1979) it is known that one species of lignin degrades rapidly even at low temperatures, thus indicating a minimum of three species. The Purdue family, however, only includes two lignin species. Previous studies (e.g. Andersson et al. 2002b; Gustavsson and Al-Dajani 2000; Lindgren 1997) show that one state per carbohydrate component is insufficient exposing a further deficiency in the Purdue model structure.

The 3-stage family models suffer from the abrupt transitions between initial, bulk and residual stages. These are hard to justify given the data presented in Fig. 1. It is also known from (Lindgren 1997, p. VII:9) that the carbohydrate degradation is not directly linked to the delignification kinetics. A third disadvantage is that the 3-stage models do not model the individual hemicelluloses which is needed to predict the properties of the final pulp (Molin and Teder 2002). Finally, the abrupt model transitions can cause numerical difficulties in off-line optimisation studies (Andersson et al. 2002a).
The model proposed by Lindgren and Lindström (1996) for the amount of slow-reacting lignin depending upon the conditions of the cook comes closest to reproducing the data given in Fig. 2. It is, however, inapplicable for the industrially important case with varying liquor composition profiles. The failure of any of the established models to adequately predict recent cooking data gives the motivation to develop an improved kinetic model.

(a) Autoclave cooks with constant [OH⁻], according to the Purdue model.

(b) Autoclave cooks with a step change in [OH⁻], according to the Purdue model.

(c) Autoclave cooks with constant [OH⁻], according to the 3-stage model.

(d) Autoclave cooks with a step change in [OH⁻], according to the 3-stage model.

Fig. 2. Commonly employed kinetic models compared to autoclave experiments at varying [OH⁻] levels (Lindgren and Lindström 1996). Upper: The Purdue model (Christensen et al. 1983), Lower: The 3-stage model (Gustafson et al. 1983).
Delignification kinetics

To establish a more general model that describes the delignification kinetics during conditions of varying alkali concentration we propose that three lignin species are used, each with the general rate expression

$$\frac{dL_i}{dt} = k_i [\text{OH}^-]^r [\text{HS}^-]^s L_j$$

for $j = \text{species } 1, 2 \text{ and } 3$. (5)

This model structure with parallel reactions is derived from the Purdue model and is only valid for kraft cooking conditions, i.e. where $[\text{HS}^-] > 0$.

In the special case of constant composition cooks (constant $[\text{OH}], [\text{HS}^-], \text{ion strength, and temperature}$), the degradation trends for $L_1$, $L_2$ and $L_3$ are straight lines when plotted on a log/linear plot given first-order kinetics as shown in Fig. 3, adapted from Lindgren and Lindström (1996). The sum of the three species corresponds to the total amount of lignin.

Fig. 3. Schematic trends for $L_1$, $L_2$ and $L_3$ for a constant concentration softwood kraft cook.

A first attempt to quantify the proportion of the lignin species $L_2$ and $L_3$ was proposed by Gustavsson et al. (1997) who develop an expression involving the amount of $L_1$ (termed residual phase lignin in the original publication) at $t = 0$ as a function of $[\text{OH}]$ and $[\text{HS}^-]$, but independent of temperature. The problem, noted in the original work, is that this model does not account for any subsequent changes in alkali rendering it of limited value for industrial cooking conditions.

The reasoning behind the proposed mechanism to incorporate varying alkali conditions is the observation in Fig. 2 that the level at the intersection of the asymptotic data for species 2 and 3 depends on the cooking conditions as shown schematically in Fig. 4. As will become evident in the description below, the intersection is in fact the lignin level where $L_2 = L_3$ and is termed $L^*$ in the following development. Moreover, this intersection, $L^*$, is at the same level of lignin for the same alkali concentration, irrespective of when it occurs in the cook.
Fig. 4. Schematic showing the dependence of $L^*$, (o), on cooking conditions, here [OH].

Extracting the intersections from Fig. 4 and plotting them against [OH], [HS$^-$], and temperature gives Fig. 5. A multi-variable curve fit, assuming no cross-coupling terms, gives an expression for $L^*$ as a function of the surrounding conditions

$$L^* = 0.49 ([\text{OH}^-] + 0.01)^{-0.65} ([\text{HS}^-] + 0.01)^{-0.19} (1.83 - 2.91 \times 10^{-4} (T - 273.15))^2$$  

(6)

Fig. 5. $L^*$ as function of [OH$^-$], [HS$^-$], and T. Data from analysis of Lindgren and Lindström (1996).

The algorithm to determine the proportions of $L_2$ and $L_3$ lignin proceeds as follows and is depicted schematically in Fig. 6. At any instant in the cook $t_0$, assuming the current cooking conditions are maintained for the foreseeable future, the reaction rates for $L_2$ and $L_3$ correspond to lines with known slopes from the kinetic expressions in Eqn. 5. Using the regressed parameter values from Table 1, these rate expressions are

$$k_{L_2} = 0.10 e^{\frac{127000}{R} \left( \frac{1}{443.15} - \frac{1}{T} \right)} [\text{OH}^-]^{0.68}[\text{HS}^-]^{0.39}$$  

(7)

$$k_{L_3} = 0.0047 e^{\frac{127000}{R} \left( \frac{1}{443.15} - \frac{1}{T} \right)} [\text{OH}^-]^{0.2}$$  

(8)
Fig. 6. Schematic illustration of how the proportions of $L_2$ and $L_3$ are computed given a step change in $[OH]$. These lines intersect at time $t(L^*)$. The current amount of $L_2$ and $L_3$ at $t_0$ can then be back-calculated by

$$L_2 = L^* e^{-k_2 \Delta t}, \quad L_3 = L^* e^{-k_3 \Delta t}$$

(9)

where $\Delta t$ is defined as $t(L^*) - t_0$. Substituting Eqn. 9 into the mass balance for lignin

$$L - L_1 = L_2 + L_3$$

(10)

gives an implicit relation for $\Delta t$ as

$$L - L_1 = L^* (e^{-k_2 \Delta t} + e^{-k_3 \Delta t})$$

(11)

which can be solved for $\Delta t$ using any standard numerical nonlinear equation solver. The current amounts of $L_2$ and $L_3$ can now be computed from Eqn. 9. This distribution model assumes that there is no interchange between $L_1$ and the other lignin species which is supported by Kondo and Sarkanan (1983). This procedure must be computed every integration time step, or at least every step when the alkali or temperature changes.

A graphical interpretation of the model referring to Fig. 6 is as follows. At any particular time during the cook, one can compute the instantaneous slopes of the $L_2$ and $L_3$ degradation reactions, and the lignin level where $L_2$ and $L_3$ will eventually be equal, $L^*$. One does not know the current value of $L_2$ or $L_3$ due to the possible changes in alkali level, nor when $L^*$ will occur. However introducing the necessary condition that $L_2 + L_3$ sum to a known lignin level, and that the intersection occurs at the level of $L^*$, the problem is well-posed and has a unique solution.

A physical-chemical interpretation of the model assumes that the two species of lignin, $L_2$ and $L_3$, interchange reversibly and, compared to the degradation reactions, instantaneously. This $L_2 \leftrightarrow L_3$,
equilibrium is assumed dependent on alkali and temperature, and the liquor composition dependence has been previously hypothesised (Lindgren and Lindström 1996; Teder and Olm 1981).

**Validation of the proposed kinetic model**

In Lindgren and Lindström (1996), the true cooking time is converted to time at 170°C using an apparent activation energy of $E_a = 134$ kJ/mol as suggested by Vroom (1957). However, in the present analysis, to avoid unnecessary assumptions and to improve the fitting of parameters, the true cooking time was used. Consequently the raw data from Lindgren and Lindström (1996) was back-converted to true time for use in the plots presented in this work. When calculating the models, it was assumed that the given set temperature profiles were maintained, and that the liquor composition changed according to the consumptions given.

Fig. 7(a) compares the proposed model with regressed parameters given in Table 1 to the data from Lindgren and Lindström (1996) for four cases where [OH] is held constant (after an initial impregnation stage). It is evident that the proposed model's quality of prediction is comparable to the model developed by Gustavsson et al. (1997) and Lindgren and Lindström (1996). However, the key contribution of this model is its ability to also predict the data in the cases where [OH] is changed. Fig. 7(b) compares the proposed model's predictions in the cases where [OH] is abruptly changed part-way through the cook. The data and dashed lines for the cases where [OH] is held constant are retained in Fig. 7(b) for comparison.

Fig. 8 reinforces the hypothesis that the proportions of $L_2$ and $L_3$ (or equivalently $L^*$) are dependent on [HS']. For step changes in [HS'], the model will respond in a similar manner to that observed for [OH], although much less pronounced. In fact, when $L_3$ is much larger than $L_2$, an increase in [HS'] results in a negligible effect on the lignin degradation, hence supporting the observation in Lindgren and Lindström (1996). While the influence of [HS'] was less compared to that of [OH], the effect of temperature was even smaller as shown in Fig. 9. In fact, Lindgren and Lindström (1996) assume that the initial concentration of $L_3$ (termed $L_3$, which plays a similar role as $L^*$ in this model) is independent of the cooking temperature. Notwithstanding, the present work retained the influence of temperature on $L^*$, since the fit improved slightly when incorporating the effect of temperature, particularly for the $T = 180°C$ series. What did change significantly, was the regressed value for the activation energy for $L_3$. Keeping the temperature influence of $L^*$ gave a value of $E_a = 127$ kJ/mol (intriguingly close to the fitted value for $L_2$), otherwise $E_a = 144$ kJ/mol. Further data is needed at longer cooking times to better resolve this dilemma given the importance of the activation energy for temperature selectivity.
(a) Total lignin (solid), and lignin species $L_1$, $L_2$, $L_3$ (dashed) at different constant $[\text{OH}^-]$ levels.

(b) Upper: Lignin trend (solid) for a step increase in $[\text{OH}^-]$ from 0.1 to 0.9 M (dashed line is for constant $[\text{OH}^-] = 0.1$ M). Lower: Lignin trend (solid) for a step decrease in $[\text{OH}^-]$ from 0.9 to 0.1 M (dashed line is for constant $[\text{OH}^-] = 0.9$ M).

Fig. 7. Model predictions of an autoclave cooking scheme. Data from Lindgren and Lindström (1996).
The proposed lignin model was validated using multiple series of laboratory autoclave and circulation cooks neither used for the model development, nor parameter fitting. Fig. 10 shows the good agreement between model and data from one series of autoclave cooks, despite possible inconsistencies between the different cooking studies, wood characteristics, etc. It should be noted that the difference between the free and the bound liquor portions was significant, at least during the initial period of the cook, and that the [OH] and [HS] of the bound portions should be used in the kinetic expressions and distribution model.

The performance of the model for an even more realistic cooking profile is given in Fig. 11, duplicating a modified cooking scheme, ITC (Andtbacka and Tibbling, 1994), in a circulation digester. A single offline analysis of the final pulp is shown for comparison. For both validation scenarios, it is interesting to note the
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$L_0$ level changing as the surrounding alkali changes, even increasing in the initial period of the cook when the [OH] decreases.

Whilst the ion strength of the liquor is known to influence delignification kinetics, this is not considered in the present model, although suitable expressions can be added to the relevant kinetic expressions and the distribution model when fully characterised. Note, however, that all data used for model building and validation were at similar ion strength levels. Furthermore, reasonable variations of ion strength around the nominal value used in this study of $[Na^+] = 1.5$ M are shown in Lindgren and Lindström (1996) to have only a slight influence.

In summary, the justification for using the more complex proposed model is most evident in the improved fit for the cases with varying alkali shown in Fig. 7 compared to the more commonly employed models such as the Purdue model shown in Fig. 2 for the same data. Note that the only increase in complexity to the model proposed by Lindgren and Lindström (1996) is the hypothesised temperature dependence of $L^*.$

![Graphs showing lignin and [OH] concentration over time and temperature profile](image)

Fig. 10. Model predictions for an autoclave cooking scheme. Upper: Total lignin (solid), and species $L_1$ - $L_0$ (dashed), Middle: $[OH]$, free (dashed) and bound (solid), and Lower: temperature profile. Data from this study.
Carbohydrate kinetics

The number of studies on carbohydrate reaction kinetics is limited compared to those on lignin. Of the few published models (Christensen et al. 1983; Gustavsson and Al-Dajani 2000; Lindgren 1997; Pu et al. 1991; Saltin 1992; Smith 1974; Wisnewski et al. 1997), many are contradictory with, for example, very different activation energies and very different native proportions of the various carbohydrate components.

In the proposed model, the carbohydrates are divided into three components: cellulose and two hemicelluloses, glucomannan and xylan. The carbohydrate trends in Fig. 12 show that they were degraded to very different extents, following different dynamics. As in the lignin model, these three components are further divided into three species. This is justified by the dissolution pattern most evident in xylan in Fig. 12, which exhibits an initial rapid degradation at low temperature, followed by a levelling out despite the increase in cooking temperature. As the temperature increased still further, new reactions took place again resulting in increased dissolution (refer Fig. 10), illustrating the cooking conditions employed. Eventually, this period of the cook levelled out, and a comparatively low reaction rate was observed during the final part of the cook. Using three carbohydrate species per component is believed to be unique. Still the existence of slow-reacting carbohydrate species evident from the long cooks by Lindgren (1997), and the findings pertaining to the easily dissolved carbohydrates (Kondo and Sarkanen 1983; Olm and Tistad 1979) support this model structure.
Fig. 12. Autoclave cooking pulp composition trends for (Upper) cellulose and glucomannan and (lower) xylan and lignin. All lines are profiles according to the proposed model. Cooking conditions according to Fig. 10.

The proposed structure for the carbohydrate kinetics is

$$\frac{dW_0}{dt} = -k_1 \left( [OH^-]^b + k_2 \right) W_0$$  \hspace{1cm} (12)

for the three components, (i), cellulose, glucomannan and xylan, each with three species (j) with $k_i$ = $Ae^{-E_{act}/RT}$.

Eqn. 12 implies that the reaction rates are independent of [HS], and that $k_2$ reflects the observation of degradation even at extremely low alkali concentrations.

As in the case of lignin, the proportion of the carbohydrate species was dependent on the current alkali conditions as shown by the data from Lindgren (1997) reproduced in Fig. 13. Since no data were available for the individual carbohydrate components, only the total carbohydrates, $CH$, were considered. The intersection of $CH_2$ and $CH_3$, termed $CH^*$, was derived from the asymptotic data from Fig. 13 in a manner similar to that described for lignin. Regressing $CH^*$ against [OH] yields

$$CH^* = 42.3 + 3.65 \left( [OH^-] + 0.05 \right)^{0.54}$$  \hspace{1cm} (13)

The distribution model (the algorithm for calculating the proportion of $CH_2$ and $CH_3$) was the same as for lignin described earlier. However, in this case the rate expressions for $CH_2$ and $CH_3$ were approximated as the average of the individual rate expressions for $C_2$, $G_2$, $X_2$ and $C_3$, $G_3$, $X_3$ respectively, weighted by the current amounts of each component.
Fig. 13 (analogous to Fig. 7(a)) shows the fit to cooking data from Lindgren (1997) at different constant [OH] levels. CH* was assumed independent of temperature in Eqn. 13 which is justified by the asymptotic data trends in Fig. 14. Unfortunately no data was available at different constant [HS] levels, nor for step changes in [OH]. However it is known that the carbohydrates dissolution is independent of [HS], Lindgren (1997).

Validation of the carbohydrate model for the autoclave experiments in Fig. 12 and for the circulation cook in Fig. 15 demonstrate that the carbohydrate model, in addition to the lignin model, describes the data to an accuracy appropriate for the intended uses for offline optimisation and model-based control.

**Fig. 13.** Model predictions of total carbohydrates, (%ow), at various constant [OH] levels. Data from Lindgren (1997).

**Fig. 14.** Model predictions of total carbohydrates, (%ow), at various constant temperature levels. Data from Lindgren (1997).
Model summary and parameters

The generic structure for the kinetics appropriate for all species, $j$, of all components, $i$, is

$$\frac{dW_{ij}}{dt} = -k_1 \left( \left[ \text{OH}^- \right]^m \left[ \text{HS}^- \right]^n + k_2 \right) W_{ij} \quad (14)$$

being a combination of Eqn. 5 for lignin and Eqn. 12 for carbohydrates with $k_i = Ae^{-Ea/T}$. Table 1 lists the regressed model parameters using a weighted nonlinear least-squares optimiser, and initial conditions for this expression. Given that one cannot directly measure the individual species, the initial conditions were also treated as fitted parameters. Note, however, that the distribution model gives the initial proportions of species 2 and 3, which in turn is a function of the initial alkali concentrations and temperature. To better fit both the original data in Lindgren and Lindström (1996) and Lindgren (1997), this study modified these initial amounts slightly.

The influence of $[\text{OH}]$ and $[\text{HS}]$ stem from the studies by Kondo and Sarkanen (1983) and Olm and Tistad (1979) for species 1, and Lindgren and Lindström (1996) for lignin species 2 and 3, and Lindgren (1997) for carbohydrates species 2 and 3. In all cases, the values listed in Table 1 were re-fitted to the published data. While the reaction rate for $L_j$ was independent of $[\text{HS}]$, the amount of $L_j$ did depend on $[\text{HS}]$ via the distribution model. The carbohydrate degradations were independent of $[\text{HS}]$, as indicated in Eqn. 12, and the constant $k$ reflected the non-zero reaction rate even at very low $[\text{OH}]$ conditions.
Since Olm and Tistad (1979) found that the ratio between the lignin and carbohydrate reactions is independent on temperature for species 1, it follows that the activation energy must be similar, $E_a = 50$ kJ/mol. This relatively low value is justified given that the degradation is diffusion controlled. It should be noted that the activation energy of $E_a = 169$ kJ/mol for CH$_3$, i.e. carbohydrates species 3, given by Lindgren (1997) holds for the viscosity loss, but not for the yield loss. After appropriate re-working, this value corresponds to 145 kJ/mol, which is close to the proposed 144 kJ/mol given in Table 1.

The pre-exponential factors, $A_i$ in Table 1 were derived from the data of Lindgren and Lindström (1996) and Lindgren (1997) using unrealistically high liquor to wood ratios. These values were modified by the factor in Table 1 when considering the autoclave and circulation digester data from this study. The factors for degradation of species 3 is less than or equal to 1 reflecting that this reaction is known to be hampered by the increased concentration of dissolved organic matter (Blixt and Gustavsson 2000). Equivalently the same study proposes that the species 2 reaction rates are increased. The large factors for CH$_3$ primarily reflects the difficulty in accurately determining this data from the few data points in the initial period given by Lindgren (1997).

A stoichiometric balance for the consumption of cooking chemicals was applied to model the autoclave and circulation digester cooks using realistic liquor to wood ratios. This was accompanied by Fick’s law diffusion model to predict both bound and free liquor concentrations as shown in Fig. 10.

**Table 1. Model parameters, used in Eqn. 14.**

<table>
<thead>
<tr>
<th>Component</th>
<th>% ow ($t = 0$)$^a$</th>
<th>powers</th>
<th>const</th>
<th>pre-exp $A^c$ factor</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_1$</td>
<td>9.0</td>
<td>0.1</td>
<td>0.06</td>
<td>0.10</td>
<td>50</td>
</tr>
<tr>
<td>$L_2$</td>
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<tr>
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<td>6.4*10$^{-4}$</td>
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<td>0.060</td>
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<tr>
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<tr>
<td>$X_1$</td>
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<td>0.42</td>
<td>6.4*10$^{-4}$</td>
<td>0.4</td>
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</table>

$^a$Species 2 and 3 are dependent on cooking conditions.


$^cA = A \exp(E_a/(R-443.15))$

$^d$If $L^k = f(T)$, else 144 kJ/mol.

**Conclusions**

This work describes a new model for the kinetics of kraft cooking. The underlying kinetic expressions are similar to those used in the Purdue model, as is the assumption of parallel reactions. The concept of using a
transition point which is a function of the environmental conditions (alkali and temperature) in the distribution model is similar in thinking to the 3-stage model. In summary, the proposed model is a hybrid of both established model families for kraft cooking.

This model, in contrast to all prior models, fits autoclave and circulation digester data, including the industrially important cases with varying alkali and temperature profiles during the cook. Consequently the model is appropriate for both offline optimisation studies and for online model-based control applications. It is suitable for kraft cooking with, or without, an impregnation stage using cooking temperatures from 150°C to 180°C. Valid operating conditions are 0.1 M to 1 M for [OH⁻], 0.05 M to 0.6 M for [HS⁻], and ion strength around [Na⁺] = 1.5 M.

However, the improved performance of the proposed model comes at the cost of introducing more model states. In total 4 components are tracked (lignin, cellulose, and two hemicelluloses) each with 3 species giving 12 states in total. The model includes a mechanism for determining the distribution of lignin and carbohydrate species 2 and 3 as a function of the cooking conditions. The implicit nature of this expression introduces a nonlinear algebraic expression which must be solved at every integration time step, further increasing the model complexity.

Acknowledgements
The authors are grateful to Claes Lysén and the personnel at the laboratories at Kvarner Pulp AB, Karlstad, Sweden for their help and support. The financial support from the Knowledge Foundation (KK-stiftelsen) is gratefully acknowledged.
# List of symbols

<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>DESCRIPTION</th>
<th>UNITS</th>
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<tr>
<td>ow</td>
<td>time</td>
<td>on wood</td>
</tr>
<tr>
<td>t</td>
<td></td>
<td>min</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>K, °C in plots</td>
</tr>
<tr>
<td>R</td>
<td>gas constant</td>
<td>kJ/(mol·K)</td>
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<tr>
<td>$E_a$</td>
<td>activation energy</td>
<td>kJ/mol</td>
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<tr>
<td>A</td>
<td>pre-exponential factor</td>
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<tr>
<td>[OH$^-$]</td>
<td>conc. of hydroxide ions</td>
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</tr>
<tr>
<td>[HS$^-$]</td>
<td>conc. of hydrosulfide ions</td>
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<tr>
<td>$W_j$</td>
<td>Species $j$ of wood component $i$</td>
<td>kg</td>
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<tr>
<td>L</td>
<td>Lignin</td>
<td>kg, % ow</td>
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<tr>
<td>CH</td>
<td>Carbohydrates</td>
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<td>C</td>
<td>Cellulose</td>
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<tr>
<td>G</td>
<td>Glucomannan</td>
<td>kg, % ow</td>
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<tr>
<td>X</td>
<td>Xylan</td>
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<td>$k_1$, $k_2$</td>
<td>rate constants</td>
<td>e.g. M$^{-1}$min$^{-1}$</td>
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</table>
References


