This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Nieminen, Kaarlo; Sixta, Herbert

Comparative evaluation of different kinetic models for batch cooking: A review

Published in:
Holzforschung

DOI:
[10.1515/hf-2011-0122](https://doi.org/10.1515/hf-2011-0122)

Published: 01/10/2012

Document Version
Publisher's PDF, also known as Version of record

Please cite the original version:
Nieminen, K., & Sixta, H. (2012). Comparative evaluation of different kinetic models for batch cooking: A review. *Holzforschung*, 66(7), 791-799. <https://doi.org/10.1515/hf-2011-0122>

Review

Comparative evaluation of different kinetic models for batch cooking: A review

Kaarlo Nieminen* and Herbert Sixta

Department of Forest Products Technology, Aalto University
School of Science and Technology, Espoo, Finland

*Corresponding author.

Department of Forest Products Technology, Aalto University
School of Science and Technology, Espoo, Finland
E-mail: Kaarlo.Nieminen@aalto.fi

Abstract

The purpose of this study was to review some of the existing models for delignification in kraft cooking. Data and results from earlier studies were utilized to evaluate the performance of the models of Gustafson (M_G), Purdue (M_P), Andersson (M_A) and Bogren's method "continuous distribution of reactivity" (M_{Bcdr}) in terms of their ability to give a realistic description for delignification of softwood and hardwood. The M_G , M_P and M_{Bcdr} were tested on lignin data obtained from cooks of *Eucalyptus globulus*. In this case, M_P seemed to perform best, whereas the M_{Bcdr} failed in the range of low residual lignins. M_A considers the lignin subunits with various reaction speeds, and this feature improves the performance in the case of low residual lignins and helps to reflect sudden changes in cooking conditions, but the difference to the ordinary M_P is moderate.

Keywords: Andersson model; delignification; Gustafson model; kinetic model; kraft cooking; lignin subcomponents with various reactivity; model of continuous distribution of reactivity; Purdue model.

Introduction

Wood cell wall is a natural composite of the biopolymers cellulose, hemicelluloses, and lignins. In chemical pulping processes, wood chips are cooked in a digester together with the chemicals to produce a fibrous mass (pulp). Sulphite or sulphate-type pulpings are the most common. The sulphite process works in aqueous solutions of hydrogen sulphite and sulphur dioxide, and the cations can be magnesium, sodium, ammonium or calcium. The digestion occurs in sulphate (or kraft) process in sodium hydroxide and sodium sulphide. At present, the kraft process is the dominant one for several reasons. Traditionally, the alkaline cook is divided into three parts, each with kinetic characteristics of its own (Teder 2007). During the initial part, delignification is fast, but also a substantial amount of carbohydrates is degraded. During

the slow bulk delignification, most of the lignin is removed due to the long reaction time. Here, the selectivity is higher than in the initial phase, i.e., more lignin is removed than carbohydrates. In the residual delignification, all reactions are slowed down – also those for carbohydrate elimination – and the selectivity is worsened. Thus, from the point of view of maximizing the carbohydrate yield, it is favourable to stop the cooking before reaching the residual delignification. The chemical reactions during delignification are highly complex and are still not understood in all details (Pothast 2008).

A realistic mathematical model of the batch pulping process must contain the equations describing several different physical and chemical phenomena, such as flows of liquid and heat in the reactor, diffusion of chemicals into the chips as well as the chemical reactions related to delignification and carbohydrate degradation. The present work is dealing with modelling of the reaction kinetics of delignification. The purpose is to answer the question: Which kinetic models give a reliable description of the experimental delignification? In the best case, the model could support a simulation program of the cooking process. Computational aspects have also to be taken into consideration: a too complex model would slow down the simulation.

Review of the kinetic models

An array of different kinetic models of delignification has been suggested since the first half of the 20th century. The Vroom's H-factor model belongs to the first ones (Vroom 1957). In this, the temperature and cooking time are combined through integration to a single variable, the H-factor, expressing the extent of cooking. The degree of delignification is then given as an empirical function of the H-factor and the initial concentration of alkali. The function contains parameters that have to be updated with changing cooking conditions. Though the H-factor model is widely accepted, it describes the reaction kinetics insufficiently (Rantanen 2006). More complex models consider various phases of the degradation of the various wood components with different reaction kinetics. Kleinert (1966) attributed different reaction rates to the bulk and the residual phases of delignification. The reactions involved were assumed to be of first order and depending on temperature and alkali level. Wilder and Daleski (1965) adopted the Arrhenius equation to describe the temperature dependence of the reaction kinetics. LéMon and Teder (1973) confirmed that the delignification rate was of first order in lignin content. They also modelled the effect of alkali and sulphide concentrations. In the following, four of the descendants of these early models will be revisited. The models in discussion are listed in Table 1.

Model 1: Gustafson model (M_G)

In the Gustafson model (M_G), the cooking time is divided into the initial, bulk and residual stages, according to the amount of remaining lignin in the pulp (Gustafson et al. 1983). The lignin level that marks the transition from the initial to the bulk stage is set at 22.5% of lignin in softwood and the transition level from the bulk stage to residual stage at 2.2%. In all three stages, the rate of carbohydrate degradation is proportional to the delignification.

Initial stage, lignin content >22.5%:

$$\begin{cases} \frac{dL}{dt} = -k_1 \sqrt{T} L \\ \frac{dCH}{dt} = c_1 [\text{OH}^-]^{0.11} \frac{dL}{dt} \end{cases} \quad (1)$$

Bulk stage, lignin content between 22.5% and 2.5%:

$$\begin{cases} \frac{dL}{dt} = -(k_{2a} [\text{OH}^-] + k_{2b} [\text{OH}^-]^{0.5} [\text{HS}^-]^{0.4}) L \\ \frac{dCH}{dt} = c_2 \frac{dL}{dt} \end{cases} \quad (2)$$

Residual stage, lignin content <2.5%:

$$\begin{cases} \frac{dL}{dt} = -k_3 [\text{OH}^-]^{0.7} L \\ \frac{dCH}{dt} = c_3 L \end{cases} \quad (3)$$

In the above equations, L is for lignin and CH is for carbohydrate contents, $[\text{OH}^-]$ is the hydroxyl concentration, $[\text{HS}^-]$ the sulphide concentration and T is the absolute temperature. The coefficients k_1 , k_{2a} , k_{2b} and k_3 are Arrhenius expressions

$$k = A e^{-E_a/RT}, \quad (4)$$

where E_a is the activation energy of the corresponding reaction and R is the gas constant.

Pu et al. (1991) modified the Gustafson model by differentiating between cellulose and hemicelluloses concerning the CH moiety. The authors also assumed that parts of the CH are nonreactive. Further, the number of stages of the CH kinetics was reduced to an initial stage and a bulk stage. As for the other kinetic models, the M_G was mostly applied

to softwoods. Teder and Olm (1980) and Olm et al. (1988) found that in the case of eucalyptus, only young wood could be modelled with three consecutive phases of the traditional model, whereas for old eucalyptus wood, a preliminary phase, characterized by a very rapid delignification, should be added before the initial phase.

Model 2: Purdue model (M_P)

The kinetic part was only one aspect of the original M_P formulated by Smith and Williams (1974), which was developed for the simulation and control of a Kamyr digester by approximating the entire digester by a series of continuously stirred-tank reactors, modelling also the flows of liquor and heat at the reactor level.

In the M_P , the same kinetic equations are valid throughout the cook, but the different wood components are assumed to consist of fast- and slow-reacting subcomponents. Some authors refer to the subcomponents as “species” with various reactivities (Andersson et al. 2001). In its original version, only the lignin was considered to consist of two subcomponents with different reaction speeds, whereas each of the other wood components – cellulose, glucomannan and xylan – were thought to be uniform with regard to reactivity. Subsequently, the model was developed by adding non-reactive subcomponents for each main wood component. The rate of degradation was then expressed as:

$$\frac{dW}{dt} = -(h[\text{OH}^-] + k[\text{OH}^-]^a [\text{HS}^-]^b) \cdot (W - W_0) \quad (5)$$

where W is the wood component, h and k are rate constants and W_0 is the unreactive portion of the wood. Lindgren and Lindström (1996) and Lindgren (1997) modelled delignification based on three lignin reactions: a fast, an intermediate and a slow one, each associated to its own subcomponent of the lignin. Andersson et al. (2001) extended the three-reaction type concept to the other wood components. The concentration of sodium ions is also thought to have some effect on the degradation processes and was included into a M_P type by Bogren (2008).

The M_P with four wood components, each consisting of three subcomponents having different reaction speeds:

$$\begin{aligned} W &= W_1 + W_2 + W_3 \\ \frac{dW_i}{dt} &= -k_i [\text{OH}^-]^{a_i} [\text{HS}^-]^{b_i} [\text{Na}^+]^{c_i} W_i, \quad i=1,2,3 \end{aligned} \quad (6)$$

Table 1 Delignification models investigated in this work.

Model no., Lit., ^a Abbreviation	Principal author	Reaction types	Lignin subcomponents ^b
1, M_G	Gustafson	Consecutive	1
2, M_P	Purdue	Parallel	2–3
3, M_A	Andersson	Parallel	3
4, M_{Bcdr}	Bogren	(Parallel), “continuous distribution reactivity”	(Infinite)

^a1: Gustafson et al. (1983); 2: Smith et al. (1974); 3: Andersson et al. (2003); 4: Bogren et al. (2008).

^bAccording to the reaction speed during delignification.

Here, the W is any of the wood components, lignin, cellulose, glucomannan or xylan, W_1 , W_2 and W_3 are the subcomponents with fast-, intermediate- and slow-reaction types. The k coefficients are Arrhenius expressions, and the powers of the concentrations a , b and c are constants that have to be determined experimentally. The differential equations in (6) imply a certain simplification of the original kinetic equations of the M_p , and they can be applied only for kraft cooking conditions, when $[\text{HS}^-] > 0$.

Model 3: Andersson model (M_A)

Andersson (2003) and Andersson et al. (2003) improved the M_p by working with three types of reactivities for each component. The authors also considered the interchange between the intermediate- and the slow-reaction steps. Initially, the wood contains more of the lignin reacting with an intermediate speed than of the slowly reacting lignin. Because of the difference in reaction speed, at some stage, there will be equal amounts of these two lignin portions. The experimental observation was that the intersection level depends on the amounts of hydroxyl and sulphide groups as well as on the temperature in a regular way. The expression was derived for the intersection level L^* by means of a multivariable curve fit:

$$L^* = 0.49 ([\text{OH}^-] + 0.01)^{-0.65} ([\text{HS}^-] + 0.01)^{-0.19} (1.83 - 2.91 \cdot 10^{-5} (T - 273.15)^2) \quad (7)$$

It is then possible to calculate the time, at which the intersection level is reached by solving the nonlinear equation:

$$L - L_1 = L^* (e^{-k_1 [\text{OH}^-]^a [\text{HS}^-]^b \Delta t} + e^{-k_2 [\text{OH}^-]^c [\text{HS}^-]^d \Delta t}) \quad (8)$$

for Δt . In other words, changes in the cooking conditions can be taken into account by recalculating the amounts of lignin reacting with moderate and slow speed by means of equations (7) and (8). The main objective of including the lignin type “interchange” in the M_A is to reflect more swiftly the changes in the cooking conditions. Similar expressions for intersection levels are also introduced for the other wood components.

Model 4: Bogren's “continuous distribution of reactivity” model (M_{Bcd})

The Kohlrausch relaxation function (KRF, or the stretched exponential function) is frequently the adequate empirical tool to model deviations from simple exponential behaviour in time in case of studying complex systems. KRF is a generalization of the exponential function with a stretching parameter γ .

$$L(t) = L_0 e^{-(t/\tau_0)^\gamma} \quad (9)$$

The parameter τ_0 has the dimension of time. In the context of delignification, the constant L_0 in equation (9) represents the original amount of lignin. When the values of γ are between 0 and 1, the graph of the KRF appears as stretched in the horizontal direction compared to the exponential function.

The KRF is the solution of the modified kinetic differential equation:

$$\frac{dL}{dt} = -\frac{\gamma}{\tau_0^\gamma} t^{\gamma-1} L \quad (10)$$

where L can be the amount of lignin. Thus, delignification modelled by the KRF can be interpreted as having first-order kinetics with a time-dependent rate coefficient:

$$k(t) = \frac{\gamma}{\tau_0^\gamma} t^{\gamma-1} \quad (11)$$

This form of rate coefficient was proposed by Kopelman (1988) to describe reaction kinetics in porous geometry, where the reactants are spatially constrained.

Another interpretation of the KRF is as a superposition of simple exponential functions:

$$e^{-(t/\tau_0)^\gamma} = \int_0^\infty H(k) e^{-kt} dk \quad (12)$$

With this interpretation, the wood component in question is thought to consist of a continuous distribution of subcomponents with various reactivities, where $H(k)$ is the probability density distribution for the reaction rate k . The right-hand side in equation (12) is the Laplace transform of $H(k)$. Hence, the $H(k)$ can, at least in principle, be calculated by taking the inverse transform. Based on the Bromwich integral formula, it can be shown according to Pollard (1946) and Berberan-Santos et al. (2005) that:

$$H(k) = \frac{\tau_0^\gamma}{\pi} \int_0^\infty e^{(-k\tau_0 u - u^\gamma \cos(\gamma\pi))} \sin(u^\gamma \sin(\gamma\pi)) du \quad (13)$$

The shape of the distributions can be obtained by numerically integrating equation (13). Because of rapid oscillations of the integrand, the integral is difficult to compute for small values of k . Berberan-Santos et al. (2005) provide a similar integral, better suited for the small values of k . In Figure 1, the H distribution $H(k)$ is shown for different values of β .

The expression on the right-hand side of equation (9), when divided by L_0 to obtain the value 1 at $t = 0$, can be interpreted as the complementary cumulative distribution of lifetime. As it cannot be negative, the mean lifetime can be calculated by integrating the complementary cumulative distribution starting from zero:

$$\bar{\tau} = \int_0^\infty e^{-(t/\tau_0)^\gamma} dt = \frac{\tau_0}{\gamma} \Gamma\left(\frac{1}{\gamma}\right), \quad (14)$$

where Γ denotes the gamma function:

$$\Gamma(y) = \int_0^\infty e^{-x} x^{y-1} dx \quad (15)$$

It can be observed when $\gamma=1$, and when the KRF is restored to the familiar exponential function that the mean

Figure 1 Distribution of rate constants associated with the stretched exponential function. The number next to each curve is the value of the stretching parameter γ .

lifetime $\bar{\tau}$ equals the parameter τ_0 . Generally, τ_0 can be expressed as:

$$\tau_0 = \frac{\gamma \bar{\tau}}{\Gamma(1/\gamma)} \quad (16)$$

On the other hand, the mean lifetime can be calculated by an Arrhenius expression:

$$\bar{\tau} = S e^{\frac{E_a}{RT}} \quad (17)$$

The coefficient S depends on the concentrations of the ions. Inserting (17) into (16) and then (16) into (10) results in equation (18):

$$\frac{dL}{dt} = - \left(S e^{\frac{E_a}{RT}} \right)^{\gamma} \gamma^{1-\gamma} \Gamma(1/\gamma)^{\gamma} t^{\gamma-1} L \quad (18)$$

Various concentration-dependent functions S and temperature-dependent functions γ have been tried in this kinetic equation. Bogren (2008) formulated:

$$S = S_0 [\text{OH}^-]^{m+nL} [\text{HS}^-]^{o+pL} [\text{Na}^+]^{q+rL} \quad (19)$$

and

$$\gamma = \gamma_1 + \gamma_2 T, \quad (20)$$

where $S_0, m, n, o, p, q, r, \gamma_1, \gamma_2$ are parameters to be determined by a fit to data. Inserting (19) and (20) into (18), the result is:

$$\frac{dL}{dt} = - \left(S_0 [\text{OH}^-]^{m+nL} [\text{HS}^-]^{o+pL} [\text{Na}^+]^{q+rL} \cdot e^{\frac{E_a}{RT}} \right)^{\gamma_1 + \gamma_2 T} \times (\gamma_1 + \gamma_2 T)^{1-\gamma_1-\gamma_2 T} \cdot \Gamma\left(\frac{1}{\gamma_1 + \gamma_2 T}\right)^{\gamma_1 + \gamma_2 T} \cdot t^{\gamma_1 + \gamma_2 T - 1} \cdot L \quad (21)$$

Data of cooking parameters

The present study is based on experimental results and data taken from the literature. The cooking details can be found in Table 2. The concept of sulphidity is defined by:

$$S = \frac{2[\text{HS}^-]}{[\text{HS}^-] + [\text{OH}^-]} \cdot 100\% \quad (22)$$

Comparative discussion of the various models

Comparison of M_p and M_{Bcdr} for softwood

As pointed out, Bogren (2008) fitted the M_p (with three different reaction speeds) and the M_{Bcdr} model to softwood cooking data (Lit. 3 of Table 2), and the predictions of the two models are illustrated in Figure 2. Extrapolation to regions without data points is indicated with dashed lines. Bogren (2008) reported that the goodness of the two fits were almost the same. The shapes of the curves obtained from the two models are quite similar, at least within the reign of existing data points. However, for high temperatures, the relative difference between the two models is increasing with time, and M_p results in higher lignin contents. For low temperatures, the curves are diverging (less visible due to the logarithmic scales of Figure 2) at times beyond the data points. For these cooks, the M_p predicts higher levels of residual lignin than does the M_{Bcdr} .

Comparison of M_G , M_p and M_{Bcdr} for hardwood cookings

The models above (see Table 1) were fitted to the delignification data from cooks of hardwood (Lit. 4 of Table 2), and the fits

Table 2 Wood species and experimental conditions considered in the quoted papers, which were also utilized in the present study. In the cooks of Andersson, sulphidity was kept at constant 33%.

Lit. ^a	Species	Type of raw material	Temp. (°C)	Concentration			Liquor to wood ratio
				[OH ⁻] (M)	[HS ⁻] (M)	[Na ⁺] (M)	
1	Norway spruce	Screened industrial chips	150–180	0.1–0.9	0–0.6	0.6–2.6	41/1
2	Norway spruce	Screened industrial chips	150–167	0.1–0.9	Sulphidity const.	–	4/1
3	Scots pine	Wood meal, sapwood	108–168	0.1–0.8	0.1–0.8	0.4–2.9	6–7/1
4	<i>Eucalyptus</i> ^b	Screened chips from Uruguay	140–170	0.1–0.2	0.1–0.6	0.8–2.5	40/1

^a1: Lindgren and Lindström (1996); 2: Andersson (2003); 3: Bogren (2008); 4: Rutkowska (2009a). ^b*E. globulus*.

Figure 2 Simulated lignin development based on models fitted to softwood data by Bogren et al. (2008). Dashed curves indicate extrapolation. In each chart, curves for five temperatures ($^{\circ}\text{C}$) are presented: 108 $^{\circ}\text{C}$, 123 $^{\circ}\text{C}$, 139 $^{\circ}\text{C}$, 154 $^{\circ}\text{C}$ and 168 $^{\circ}\text{C}$. The higher the temperature, the more rapidly are the lignin levels decreasing. The x axes are logarithmic.

are presented in Figures 3A and 3B. The values of the parameters obtained for the different models are given in Tables 3–5. The M_P and M_G both provide reasonable fits, but the M_P describes delignification slightly better, in case of low residual lignin contents. The M_{Bcdr} seems unable to model delignification at low lignin levels of a hardwood cook. None of the tried models is fully satisfactory for the high levels of $[\text{OH}^-]$. In a simulation program, both the M_G and the M_P are easier to implement than the M_{Bcdr} due to the higher mathematical complexity of the latter.

Effect of the lignin interchange in M_A

The M_P with three parallel lignin reactions was fitted to softwood data (Lit. 1 of Table 2), and the fits are presented in Figure 4a. Andersson et al. (2003) had also fitted M_A to the same data. This model provides a slightly better performance, especially, when it comes to the accurate modelling of the profile “lignin content vs. time” at low levels of lignin content. The interchange between the two lignin subgroups with slower reaction in the model means a dependence of lignin types of cooking conditions, whereas this parameter is independent of the cooking conditions for M_P . In Table 6, it can be seen that the initial portion of slowly reacting lignin

decreases with increasing hydroxide content in the cooking liquor. When the M_P is fitted to the same data, the initial levels of the subcomponents with intermediate and slow reaction speeds are 17.4% and 2.6%, respectively, notwithstanding the different $[\text{OH}^-]$ levels.

The M_P and M_A were both fitted to cooking data from Lit. 2, which had substantial step changes in the $[\text{OH}^-]$ level. As visible in Figure 4b, M_A performed better.

Also, the *Eucalyptus* data from Lit. 4 contain cooking series with sudden (discontinuous) changes in cooking conditions. The fittings of M_P and M_A to this data (see Figure 4c) confirm the better performance of the latter.

For in-depth considerations, both M_P and M_A were applied for some hypothetical cases including a change in cooking conditions. The results are shown in Figures 5A and 5B. The differences in the predictions of the two models are not large. The susceptibility of M_P to abrupt changes is comparable to that of the M_A . In some cases (Figures 5A,b and 5B,c) of the deviation from the constant conditions, predictions are even slightly more elevated for M_P than for M_A .

Andersson (1997) and Andersson et al. (1997) found better agreement between experimental data and modelling by M_A than by M_P . But it should be remembered again, that the

Figure 3A,B Delignification models fitted to cooking data of *Eucalyptus globulus*. The solid curve represents the Gustafson model (M_G , no. 1) with two consecutive periods, the dashed line, the Purdue model (M_P , no. 2) with two lignin reactivities (subcomponents), and the dotted line, the Bogren model (M_{Bcd} , no. 4). The points represent experimental data. The x axes are logarithmic.

Table 3 Parameters of the Purdue model (M_p) when fitted to the *E. globulus* data of Rutkowska (2009b). Lignin 1 is the lignin subcomponent with fast reaction speed, and Lignin 2 is that with slow reaction speed.

Parameter	Symbol	Lignin 1	Lignin 2
Initial content (%)	λ	17.6	1.2
Activation energy (kJ mol ⁻¹)	E_a	130.6	129.7
Frequency factor (min ⁻¹)	A	1.1×10^{15}	1.4×10^{14}
Exponent [OH ⁻]	a	0.63	1.71
Exponent [HS ⁻]	b	0.33	0.53
Exponent [Na ⁺]	c	-0.58	-0.68

Table 4 Values of the parameters of the Gustafson model (M_G) when fitted to data of *E. globulus* according to Rutkowska (2009b).

Parameter	Symbol	Bulk	Residual
Initial content (%)	λ	18.9	
Activation energy 1 (kJ mol ⁻¹)	E_{a1}	66.7	171.3
Frequency factor 1 (min ⁻¹)	A_1	3.7×10^6	4.2×10^{19}
Activation energy 2 (kJ mol ⁻¹)	E_{a2}	144.7	
Frequency factor 2 (min ⁻¹)	A_2	3.87×10^{15}	

Table 5 Values of the parameters of the M_{Bcdr} when fitted to the data of *E. globulus* according to Rutkowska (2009b).

Symbol	Value	Unit
S_0	5.0×10^{14}	min ⁻¹
m	1.49	
n	-1.60	
o	0.81	
p	-0.30	
q	-0.82	
r	-0.24	
E_a	127	kJ mol ⁻¹
γ_1	-2.01	
γ_2	7.1×10^{-3}	K ⁻¹

quoted authors considered three lignin reactivities instead of two in M_p . The real importance of three lignin subgroups reacting with various speeds can only be judged by further empirical experiments.

Additional explanations to the modelling

Effective cooking time

In the heating up period of cooks, the delignification temperature is not constant. The relative length of this period cannot be neglected in the kinetic model. The problem has been handled by transforming the cooking time into “effective time”, i.e., the time at which the same amount of delignification would have occurred as at a theoretical constant temperature cook.

Figure 4 Comparison of Purdue fit (M_p , no. 2, dashed lines), the Andersson model (M_A , no. 3, solid lines) and experimental data from the literature. a) Softwood cooks (Norway spruce) of Lindgren and Lindström (1996). Constant temperature at 170°C; [HS⁻] = 0.15 M. b) The same as in a) but abrupt (discontinuous) changes in [OH⁻] levels after 140 and 233 min. c) Hardwood cooks of Rutkowska (2009b) (*E. globulus*) with abrupt (discontinuous) changes in [OH⁻] levels at 41 and 69 min. The x-axes are logarithmic.

The relation between the real cooking time and the effective time is calculated assuming that the reaction rate is an Arrhenius expression:

$$k = Ae^{-E_a/RT} \quad (23)$$

Table 6 Initial portions of lignin subcomponents for different [OH⁻] concentrations.

[OH ⁻] conc (M)	Lignin subcomponents with	
	Interm. reaction speed (%)	Slow reaction speed (%)
0.1	16.8	3.2
0.23	18.1	1.9
0.44	18.7	1.3
0.9	19.1	0.9

Figure 5 Models of Andersson (M_A) according to Anderson (2003) and Andersson et al. (2003). A) Simulated lignin decrements in cooks with an abrupt change in the chemical concentrations appearing at $t=200$ min. B) Simulated lignin decrements in cooks with an abrupt change in the temperature and chemical concentrations appearing at $t=200$ min. Solid curve: lignin decrement under unchanged conditions. Dashed curve: lignin decrement under conditions of abrupt changes in cooking conditions, which were calculated without the lignin subgroup interchange. Dotted line: lignin decrement with consideration of the lignin subgroup interchange.

with constant activation energy E_a and that the delignification with reasonable approximation can be described by the simple differential equation:

$$\frac{dL}{dt} = kL \quad (24)$$

By switching the differentials into finite differences, the equation is:

$$\frac{\Delta L}{\Delta t} = kL \Rightarrow \Delta L = Ae^{-E_a/RT} L \Delta t. \quad (25)$$

Then, the time interval $\Delta t'$, at which the same amount of delignification is achieved at the temperature T' , can be calculated from:

$$Ae^{-E_d/RT} L \Delta t = Ae^{-E_d/RT'} L \Delta t' \Rightarrow \Delta t' = e^{E_d/R(1/T' - 1/T)} \Delta t \quad (26)$$

The effective time of the cook is calculated by adding the converted time steps of the heating up time.

Consistency of the different models

Even though the various kinetic models give similar predictions for the lignin development and are in reasonable accordance with experimental data, it must be remembered that the underlying assumptions for the chemical mechanisms associated with the models are quite disparate and cannot all be valid at the same time. At present, the models can be accepted as phenomenological ones in simulation as long as extrapolation is avoided. In order to distinguish between the different kinetic models, more experiments are needed, as pointed out by Burazin (1986), under such cooking conditions where their predictions diverge.

Conclusions

1. For softwood, the Purdue model (M_p , model 2) and the Bogren model (M_{Bcdr} , model 4) are both in reasonably good agreement with the cooking data. Prolonged softwood cooks at low temperatures could help in discriminating between the M_p and M_{Bcdr} .
2. For hardwoods, the Gustafson model (M_G , model 1) and the M_p perform better than the M_{Bcdr} , especially in describing the low-lignin contents after prolonged cooks. In this region of residual lignins, there is also a small advantage for M_p over the M_G .
3. The Andersson model (M_A , model 3) offers some improvements compared to M_p , which are more visible for softwoods than for hardwoods.
4. The M_p is also able to reflect sudden changes in cooking conditions, i.e., changes occurring in discontinuous steps.

Acknowledgements

The authors want to thank Ewa Rutkowska and Niclas Andersson for their contribution and advice regarding experimental data. We are also grateful for the financial support from the PaPSaT – programme.

References

- Andersson, N. (2003) Modelling of kraft cooking kinetics using near infrared spectroscopy. Ph.D. thesis, Karlstad University, Karlstad, Sweden.
- Andersson, N., Wilson, D.I., Germgård, U., Lindström, T. (2001) Organic matter content in black liquor inside and outside chips during kraft cooking. *Pap. Puu – Pap. Tim* 83:538–541.
- Andersson, N., Wilson, D., Germgård, U. (2003) An improved kinetic model structure for softwood Kraft cooking. *Nord. Pulp Paper Res. J.* 18:200–209.
- Berberan-Santos, M.N., Bodunov, E.N., Valeur, B. (2005) Mathematical functions for the analysis of luminescence decays with underlying distributions 1. Kohlrausch decay function (stretched exponential). *Chem. Phys.* 315:171–182.
- Bogren, J. (2008) Further insights into kraft cooking kinetics. Ph.D. thesis, Chalmers University of Technology, Gothenburg, Sweden.
- Bogren, J., Brelid, H., Theliander, H. (2008) Assessment of reaction kinetic models describing delignification fitted to well-defined craft cooking data. *Nord. Pulp Paper Res. J.* 23:210–217.
- Burazin, M.A. (1986) A dynamic model of kraft-anthraquinone pulping. Ph.D. thesis, Lawrence University, Appleton, Wisconsin, USA.
- Gustafson, R.R., Snelcher, C.A., McKean, W.T., Finlayson, B.A. (1983) Theoretical model of the kraft pulping process. *Ind. Eng. Chem. Process Des. Dev.* 22:87–96.
- Kleinert, T.N. (1966) Mechanisms of alkaline delignification. I. The overall reaction pattern. *Tappi* 49:53–57.
- Kopelman, R. (1988) Fractal reaction kinetics. *Science* 241:1620–1626.
- LéMon, S., Teder, A. (1973) Kinetics of the delignification in kraft pulping I. Bulk delignification of pine. *Sven. Papperstidn.* 76:407–414.
- Lindgren, C.T., Lindström, M.E. (1996) The kinetics of residual delignification and factors affecting the amount of residual lignin during kraft pulping. *J. Pulp Paper Sci.* 22:290–295.
- Lindgren, C.T. (1997) Kraft pulping kinetics and modeling, the influence of HS-, OH- and ionic strength. Ph.D. thesis, Royal Institute of Technology, Stockholm, Sweden.
- Olm, L., Sandström, P., Teder, A. (1988) Kinetics of kraft pulping and a mathematical model for delignification as a basis for modification of kraft pulping. *O. Pap.* 49(2): 25–32.
- Pollard, H. (1946) The representation of e^{-x^k} as a Laplace integral. *Bull. Am. Math. Soc.* 52:908–910.
- Potthast, A. (2008) Chemistry of kraft cooking. In: *Handbook of Pulp*. Ed. Sixta, H. Wiley, New York. pp 164–174.
- Pu, Q., McKean, W., Gustafson, R. (1991) Kinetic model of softwood kraft pulping and simulation of the RDH process. *Appita* 44:399–404.
- Rantanen, R. (2006) Modelling and control of cooking degree in conventional and modified continuous pulping processes. Ph.D. thesis, Oulu University, Oulu, Finland.
- Rutkowska, E.W., Wollboldt, P., Zuckerstätter, G., Weber, H.K., Sixta, H. (2009a) Characterizations of structural changes in lignin during continuous batch kraft cooking of *Eucalyptus globulus*. *Bioresources* 4:172–193.
- Rutkowska, E.W. (2009b) Modified kraft cooking technologies for paper and dissolving pulp. Ph.D. thesis, Graz University of Technology, Graz, Austria.
- Smith, C.C. (1974) Studies of the mathematical modelling, simulation and control of the operation of a Kamyr continuous digester for the kraft process. Ph.D. thesis, Purdue University, West Lafayette, Indiana, USA.
- Teder, A. (2007) Kinetics of chemical pulping and adaptation to modified processes. In: *Ljungberg Textbook, Pulp and Paper Chemistry and Technology, Book 2. Pulping Chemistry and Technology*. Ed. Ek, M., Gellerstedt, G., Henriksson, G. Fibre and Polymer Technology, KTH, Stockholm. pp. 161–176.
- Teder, A., Olm, L. (1980) Extended delignification by combination of modified kraft pulping and oxygen delignification. *Pap. Puu* 63:315–326.
- Vroom, K. (1957) The H-factor: a means of expressing cooking times and temperatures as a single variable. *Pulp Paper Mag. Can.* 58:228–231.
- Wilder, H.D., Daleski, E.J.J. (1965) Delignification rate studies. Part II on a series on kraft pulping kinetics. *Tappi* 48:293–297.

Received June 21, 2011. Accepted January 30, 2012.