

# Validating continuous kraft digester kinetic models

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## Abstract

Representative families of models for the chemical kinetics of kraft pulping taken from the literature spanning the last three decades are compared using data obtained from a series of autoclave cooks and an instrumented laboratory circulation digester. The differences within families is slight, and they reasonably explain the data with fitted parameters, and more crucially, even when using original parameters. However the Purdue model arguably fits the measured data better for the more modern cooking schemes, and has the advantage that it describes the kinetics of hemicelluloses such as arabinoxylan which are needed for pulp property predictions.

## 1 Introduction and scope

In order to make paper, the unwanted lignin in the wood is separated from cellulose in the presence of hydroxide and hydrogen sulphide ions at elevated temperatures and pressures in a process known as kraft pulping. As the market demand for pulp such as that intended for fine paper, or dissolving pulps for cellulose derivatives, the incentive is to first understand the complex chemical kinetics and transport phenomena in the vessel, and second to drive it in a near optimal way to ensure the economic success of the production.

The heterogeneous chemical-physical wood and cooking liquor system, coupled with the mass transfer situation defines complex phenomena. Furthermore due to the high running costs of industrial-scale digesters, difficulties in sampling, and the large time lags, laboratory cooking studies and modern modelling tools are needed to derive kinetic models to be incorporated in model-based controllers such as described in [1].

The aim of this work is to compare previously published kinetic models of kraft cooking suitable for ad-

vanced control using experimental data from an instrumented laboratory circulation digester and a laboratory autoclave. The outline of this paper is as follows. Section 2 reviews previously published kinetic models which are subsequently compared in section 3. Section 3.2 validates the models in more modern cooking scenarios (such as iso-thermal cooking) with NIR and offline measured data. Finally some conclusions and future developments are given in section 4.

## 2 Kinetic models for Digesters

The economic operation of a continuous digester practically demands model-based control. It follows, that such a scheme, requires a model of the plant containing the following three major components: (i) a description of the chemical kinetics and diffusion at the chip scale, (ii) a description of the flows within the digester, and (iii) a description of the external configuration and auxiliary control schemes. Dividing the entire digester model in these three groups allows one to distinguish between phenomena that will remain independent of location or type of digester (continuous or batch), and that that is dependent on location and infrastructure. It also eases the portability of the models between different types of digesters, different locations, feedstocks etc. This work is concerned only with the validation of models for the first component, namely the kinetics as opposed to the transport component which is a distributed parameter process.

Three broad families of digester kinetic models appropriate for the eventual aim of operation optimisation and control are chosen as representative and are described in sections 2.1–2.3. These models are subsequently compared in section 3 and a summary of these models is given in Table 1 with the number of solid states,  $n$ , and the performance index,  $\mathcal{J}$ , defined in §3.

### 2.1 Digester models with simplified kinetics

Some investigations are more concerned with the physical flows within the digester, or how the packing degree effects the operation as opposed to the reaction kinetics, [3, 4]. Consequently these complicated flow models often use only simplified kinetics and are included to establish a base reference. Both subsequent families can be traced to the pioneering work of [2].

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**Table 1:** A summary of previously published digester kinetic models

Principal author	$n$	$\mathcal{J}_L$
Lemon/Tistad, [2, 10]	1	1.5
Johnson, [3]	1	214.3
Michelsen, [4]	1	3.0
Smith, [5]	5	65.8
Christensen, [6, 7]	5	14.3
Saltin, [8]	5	1.9
Lindström, [9]	1	5.0
Gustafson, [11]	2	16.3
Pu, [12]	3	12.9
Vanchinathan, [13]	2	8.4
Meghanathan, [14]	2	181.4

## 2.2 The Purdue model

One of the earliest complete models of kraft cooking kinetics was developed in [5], and is known as the ‘Purdue model’ and most subsequent models owe much to this development. The Purdue model assumes that 5 wood species concentration states are sufficient to describe the digester, namely high-reactive lignin, low-reactive lignin, cellulose,  $C$ , galactoglucomannan,  $GCM$ , and arabinoxylan,  $AX$ . These 5 states,  $\mathbf{x}$ , are supplemented with the concentrations of hydroxide ion,  $[\text{OH}^-]$ , and hydrogen sulphide ion,  $[\text{HS}^-]$ . This model was subsequently improved in [6] and further in [8] by introducing un-reactive components, and increasing the flexibility of the rate expression to

$$\frac{dx_i}{dt} = -(k_{1i}[\text{OH}^-] + k_{2i}[\text{OH}^-]^a[\text{HS}^-]^b)(x_i - x_{i0}) \quad (1)$$

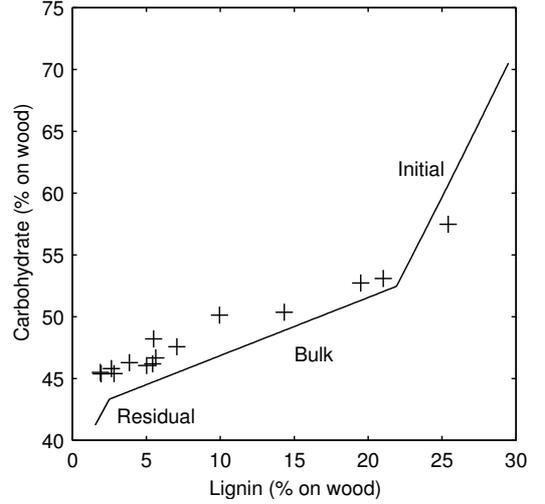
for each of the 5 states,  $i = 1, \dots, 5$ . The 10 rate constants in Eqn. 1 are expressed in Arrhenius form,  $A_i e^{-E_i/RT}$ .

From a control perspective, these models have 5 solid concentration states plus the liquor concentrations of alkali and hydrosulfide giving 7 states in total. As a first approximation the  $[\text{HS}^-]$  ion concentration can be considered constant, and the  $[\text{OH}^-]$  ion concentration can be computed from a stoichiometric balance. Furthermore, the  $[\text{OH}^-]$  can be measured online in a circulation digester, so it could be considered an input in the form of a measured disturbance.

Lindström, [9], plotted the log lignin concentration against time showing a transition in gradient part-way through the cook. This phenomena was explained by introducing an extra lignin species, where the initial concentrations were found to be dependent on the dosing of alkali.

## 2.3 The 3-stage model

Gustafson and co-workers developed a slightly different form for the kinetics in [11]. Rather than use 5 wood species states, the wood components were divided into only two: lignin, and carbohydrates. However the kinetics were more complicated by dividing the reactions into three periods: initial, bulk and residual. If the percent lignin on wood is plotted as a function of carbohydrates on wood, (as in [10, Fig 1.], reproduced in Fig. 1 with our data superimposed), then the three distinct periods are the piecewise linear lines shown on the plot.



**Figure 1:** The carbohydrate yield as a function of delignification showing 3 distinct periods as described by [11]. Superimposed are autoclave cook data.

The kinetic expression for the lignin,  $L$ , and carbohydrate,  $CH$ , are during the initial period

$$\frac{dL}{dt} = -a\sqrt{T}Le^{b/T} \quad (2)$$

$$\frac{dCH}{dt} = c_1[\text{OH}^-]^{0.11} \frac{dL}{dt} \quad (3)$$

during the bulk period starting at 22% lignin on wood,

$$\frac{dL}{dt} = -(k_{1i}[\text{OH}^-] + k_{2i}[\text{OH}^-]^{0.5}[\text{HS}^-]^{0.4})L \quad (4)$$

$$\frac{dCH}{dt} = 0.47 \frac{dL}{dt} \quad (5)$$

and during residual period,

$$\frac{dL}{dt} = e^{19.64 - 10804/T}[\text{OH}^-]^{0.7}L \quad (6)$$

$$\frac{dCH}{dt} = 2.19 \frac{dL}{dt} \quad (7)$$

starting around 1.1% to 2.5% lignin on wood. An extension to model modified cooking schemes was developed in [12] which now separates the carbohydrate into cellulose and hemicellulose, and also assumes  $[\text{HS}^-]$  is

not consumed. Two recent studies which use a simplification of the diffusion model are [13] and [14] which compliment the development using online measured data.

The disadvantage with this piecewise-linear formulation of the kinetics is that the transition points are still somewhat arbitrary, and the presence of the discontinuities is both of arguable justification (looking at the original measured data and that presented in Fig. 1), and makes it considerably more difficult to compute optimal solutions using this type of model structure.

### 3 Kinetic model comparison

All eleven models described in sections 2.1–2.3 were computed in MATLAB and compared with kraft cooking data of Scandinavian spruce (*Picea abies*) chips from a series of autoclave cooks and a series of experiments in an instrumented circulation digester equipped with an online NIR analyser. Details of the reference chemical analysis, and the potential of the NIR analyser for cooking chemicals in the liquor are given in [15, 16]. Table 1 summarises the predictive performance of the models listing the sum of squared errors of the lignin concentration,  $\mathcal{J}_L$ , using the original literature values. A small value of  $\mathcal{J}_L$  indicates that the model closely approximates the experimentally measured lignin profile.

Fig. 2 shows a broad comparison between the two principle model families; the ‘Purdue’ (§2.2) and the 3-stage model (§2.3), using the original parameters validated against part of the autoclave data. In all cases, the model predictions for lignin content, +, carbohydrate,  $\diamond$ , and lignin,  $\square$ , % on wood and the bound ( $\circ$ , dashed) and free ( $\times$ , solid) alkali, are compared with laboratory measured values. As expected the differences within families is slight, (with the exception of [14]), and even across families is small for the conventional cooking scheme illustrated here. Notwithstanding, deviations in the final lignin content of 0.01 (1%) correspond to approximately 5 kappa number units which is considered significant by the industry.

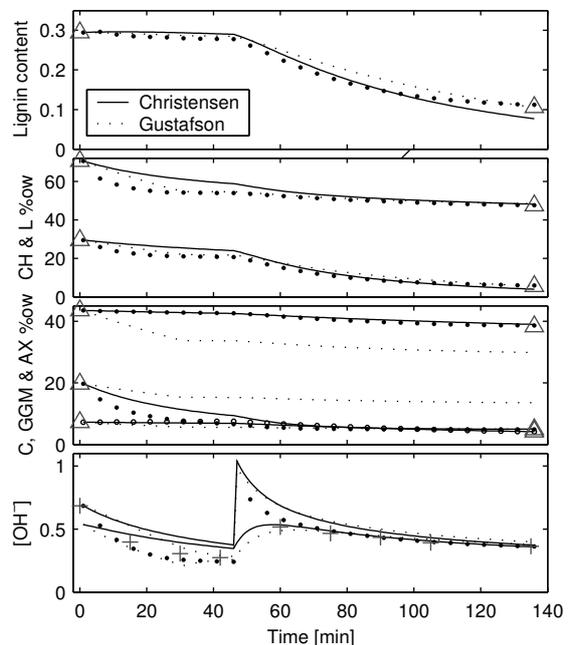
#### 3.1 Parameter optimisation

If we fit key parameters to our experimental data, as opposed to using the original literature values, one should more ably spot deficiencies in model structure. Fig. 3 shows the improvement when we fit certain key parameters of one representative model from each family, [6] and [11], both to the autoclave data from Fig. 2, and to autoclave data not plotted because they stem from different cooking schemes. While both models do adequately describe the observed profiles, Gustafson (Fig. 3(b),[11]) does not distinguish between individ-

ual carbohydrate components, but rather assumes the ratio stays the same through the cook. This simplification, clearly not supported by the measured data, has the adverse affect that the model is unsuitable for the prediction of some pulp properties such as strength and bleachability.

#### 3.2 Modified cooking schemes

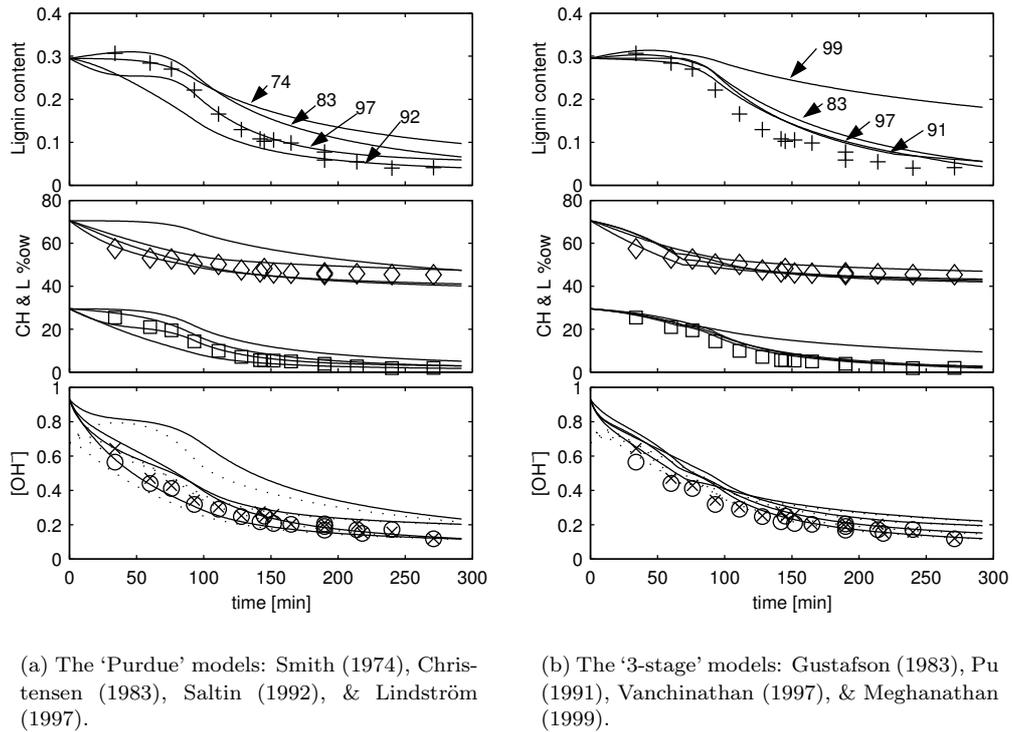
Fig. 4 compares the performance of the regressed models from §3.1 when using more modern cooking techniques with an impregnation period and a second charge of alkali intended to replicate an ITC (isothermal cooking) scheme. The NIR reference data was calculated using spectral data of the free cooking liquor combined with models, [9], that were adjusted to fit the dissolved liquor and carbohydrate concentrations (not shown in Fig. 4).



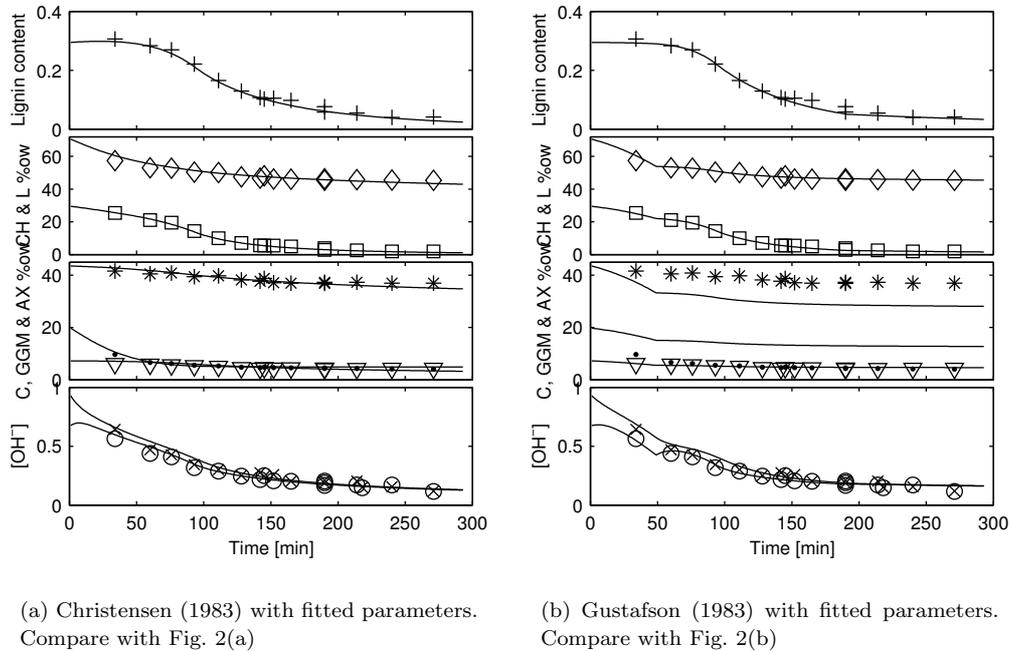
**Figure 4:** ITC cooks with pulp analysis, ( $\Delta$ ), NIR data, ( $+$ ), and with model-assisted NIR data, ( $\bullet$ ).

### 4 Conclusions

Eleven kinetic models for digesters in three broad families were compared to data collected from autoclave cooks and an instrumented circulation digester. Using the original parameters, both the Purdue and the 3-stage model families show the correct trends, although the final lignin predictions correspond to significantly different final kappa numbers. Adjusting key kinetic constants to the measured data improves the model predictions as expected, but serves to highlight the failure of the hemicellulose components for the 3-stage models. Validating the re-regressed models against data from a recent cooking scheme (ITC) exaggerates



**Figure 2:** Comparison of digester models using original parameters showing (Top) lignin content, (Middle) carbohydrate and lignin % on wood, and (bottom) alkali concentration, [mol/l].



**Figure 3:** Comparison of digester models with fitted parameters. Symbols as for Fig. 2 with the addition of (iii) cellulose (\*), galactoglucomannan, (●), and arabinoxylan, (▽) % on wood.

the ability to predict outside the conditions of the fitting. While the 3-stage model captures the end point for lignin, the Purdue model follows the trajectory better for the majority of the cook.

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