

Development of predictive oxygen delignification models using kinetic expressions and neural networks

BIBIANA R. RUBINI AND CARLOS I. YAMAMOTO

ABSTRACT: Two different methods are used to simulate the oxygen delignification reaction in a cellulose mill. One is a kinetic model that is based on models found in the literature. The other is a neural network model developed from a series of training set patterns with usual process variables as inputs and delignification reactor outlet kappa number as output. These models are a useful tool for cellulose mills once they can be applied to process simulation, optimization, and control. Moreover, different operational conditions can be tested without changing the production. Limits can be established for the main process variables so that the mill can be controlled economically without product quality loss. This study indicates that the neural network and the kinetic models present equivalent results.

Application: The models evaluated in this study may help pulp mills pretest various process variables.

To comply with environmental regulations, oxygen delignification was introduced in pulp mills in the 1970s. Oxygen delignification can reduce wastewater effluent chemical oxygen demand (COD) by 50% and biological oxygen demand (BOD) by 25%-50%, while reducing costs and bleaching chemicals amounts [1-3]. This process became predominant in modern pulp bleaching plants over the last few decades. It is expected to continue its growth as an essential part of most elemental and totally chlorine-free bleaching sequences [4].

Oxygen bleaching is a heterogeneous reaction occurring in a system comprised of fiber, alkaline solution, and oxygen. The reaction kinetics depend on reaction temperature, oxygen pressure, and alkali concentration [1,3-7]. The effects of process variables on oxygen delignification rates were first investigated by Hatler et al in 1970. Since then, several authors proposed models suggesting modifications, considering mass transfer phenomena [1-3] and fast, slow, or nonexistent lignin reaction [5-7]. None of them, however, presented an industrial application that would show the industrial efficiency of models on both simulation and control.

This study proposes kinetic models adapted from previously published equations to describe the process of an industrial delignification plant. It also proposes a neural network model for the same industrial delignification plant.

The ability to recognize and reproduce cause-effect relationships through training and filtering noise or irrelevant data,

and working with multiple input and multiple output vectors, make neural networks efficient in representing nonlinear systems [8-11]. This model offers an alternative to the kinetic models, emerging as an easy and useful industrial simulator.

KINETIC MODELS

In 1988, Hsu and Hsieh [1] published a model in which the delignification reaction was divided into two stages. At first the authors fitted the experimental data into the empirical model in one stage and obtained a high reaction order on the kappa number. Then, they suggested that this high reaction order can be caused by the sharp decrease of the delignification rate during the run and fitted the experimental data using the two-stage model:

$$-\frac{dk}{dt} = k_1 \exp\left(-\frac{E_{a1}}{RT}\right) [OH]^{1.78} P_{O_2}^{0.35} K^{3.07} [u(t) - u(t-2)] + k_2 \exp\left(-\frac{E_{a2}}{RT}\right) [OH]^{1.70} P_{O_2}^{0.74} K^{3.07} u(t-2) \quad (1)$$

The unit step function was used to imply that in the first 2 min of reaction time, the kinetic equation was described by the first term and during the rest of the reaction time it was described by the second term [1].

Agarwal et al [3] proposed a model in one stage, maintaining the high reaction order on the kappa number:

$$-\frac{dk}{dt} = k \exp\left(-\frac{E_a}{RT}\right) [OH]^{1.92} P_{O_2}^{0.53} K^{7.7} \quad (2)$$

The authors also discussed the issue of the high reaction order on the kappa

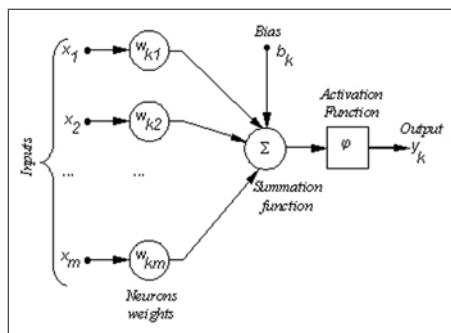
number. They brought up Schön's model [12], which pointed out that similar situations occur in petrochemical processing where high reaction rate orders were observed. These were explained in terms of many parallel first order reactions taking place simultaneously during hydrodesulfurization and hydro-denitrogenation of oil.

Agarwal et al. [3] concluded that mass transfer resistances are not responsible for the observed high order, which was explained in terms of lignin moieties having different first order reactions. Applying Schön's model and considering a great number of parallel first order reactions, Agarwal et al. improved their results greatly.

The last kinetic model selected for this work was proposed by Violette [4] in his doctoral thesis. The hypothesis of the investigation was that oxygen radicals may be trapped with relatively low amounts of additive radical scavengers if they are concentrated at the cellulosic surfaces, thereby acting as protective barriers for the cellulose. To evaluate his hypothesis, Violette did not use oxygen on his reactor, suggesting a kinetic model that did not consider the oxygen influence on the reaction.

Violette [4] used nitrogen instead of oxygen on his experiments and proposes a model using a corrected kappa number. Once this work is modeling an industrial delignification reaction, Violette's kappa number correction is not applicable. We will consider, then, Violette's model without any kappa number correction, as shown in equation 3.

PROCESS SIMULATION



1. Typical process element in a neural network.

$$-\frac{dk}{dt} = k \exp\left(-\frac{Ea}{RT}\right) [\text{OH}]^{0.588} K^{3.12} \quad (3)$$

Each of the three models has its own particularities, but all are in agreement that the reaction order on the kappa number is high. In Agarwal's model, the reaction order on the kappa number is doubled in relation to the other two models. The absence of the oxygen influence in Violette's model may make it useful for use by an industrial plant to discover if there is excess oxygen in the process.

All three models had their parameters (kinetic constants, activation energy and the reaction orders) adjusted in order to fit industrial data. Once there was no laboratory reproduction of the reaction, these parameters were obtained using a heuristic optimization algorithm. This method searched for parameter values that would provide minimum error between the predicted kappa number and the industrial unit actual kappa number. Genetic algorithm (GA) was chosen to adjust the kinetic model parameters.

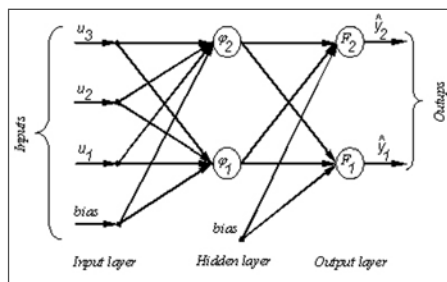
To evaluate the alkali consumption, we propose a mass balance (Eq. 4) on the reactor, which considers the alkali flow and the rate of alkali consumption.

$$-\frac{d[\text{OH}]}{dt} = \frac{F_{\text{alkali, solution}} ([\text{OH}] - [\text{OH}])}{V} - r_{[\text{OH}]} \quad (4)$$

The rate equation for the alkali consumption is given, according to Violette's model, by Eq. 5.

$$r_{[\text{OH}]} = d \cdot \Delta K + [\text{OH}] \quad (5)$$

Or, the rate of alkali consumption is a function of kappa number variation and the remaining alkali amount.



2. Neural network structure.

NEURAL NETWORK MODEL

The ability to learn from examples is one of the most distinct characteristic of the artificial neural networks. That justifies the choice of a neural network to model the relationship between process variables and final product characteristics in complex systems. The model using this method may be developed by using variables that are familiar to mill personnel and easily accessed as inputs, instead of parameters that are ordinarily measured [9-11].

Neural networks are computer programs that simulate the learning process of the human brain, in a tentative step toward imitating human intelligence. They are composed of neurons - process elements - that are highly interconnected. In the artificial brain, the neurons are set in layers and may be connected to neurons of the same or different layers through weighted summations and activated functions of different kinds [8-11]. Figure 1 illustrates a typical neuron. Figure 2 presents a neural network with three fully interconnected layers.

The ability to learn the input-output relationship is conferred to the network by the training set. A series of training patterns (input-output sets) are fed to the net and the neurons weight are adjusted to minimize the error between the given output and the net output [9-11]. The error is back-propagated through the net layers, altering weights of each connection proportionally. There are several back-propagation training algorithms available in the literature. The one used in this study is the generalized delta rule algorithm, a kind of gradient descent method that minimizes the sum of squares residual [9,11].

The net developed in this work is feed forward - meaning that the neurons signals are sent to the following layer - with one hidden layer. The activation function used was the sigmoid function.

Ordinary industrial process variables, expressed in mill regular units, were used as inputs to the net.

DATA ACQUISITION

This project was created to improve operations at Klabin's *Celulose e Papel - Unit Monte Alegre* delignification plant. Process data from January to July of 2005 were obtained from the industrial unit using process information software. Statistical treatments were applied to avoid errors and to assure that the collected data effectively represented the process being analyzed.

A total of 811 process variables patterns were used to adjust the proposed models. The patterns consisted of inlet kappa number, temperature, pulp production, reaction time (calculated using pulp production and reactor volume), alkali concentration and flow, oxygen flow and pressure, and consistency as inputs; all models predict the reactor's outlet kappa number.

The same variable patterns were applied for both kinetic and neural network models and their units are compatible to that indicated by each kinetic model. For the neural network model, data were normalized and divided into training and validation sets. All the kinetic models were integrated using the fourth-order Runge-Kutta method. The results presented for both kinetic and neural network model correspond to the results obtained for the validation set (405 patterns).

RESULTS

Figure 3 presents the results obtained with the adjustment of the Hsu and Hsieh model (from now on referred to as Model 1). The reaction orders were kept constant, but the activation energy, not; Arrhenius frequency factor, and the alkali consumption parameter () of Eq. 5 were varied using GA to fit the industrial data. The resulting kinetic equations for Model 1 are:

$$-\frac{dk}{dt} = 10 \cdot \exp\left(-\frac{10^4}{RT}\right) [\text{OH}]^{0.78} P_{\text{O}_2}^{0.35} K^{3.07} [u(t) - u(t-2)] + 16 \exp\left(-\frac{6.5 \times 10^4}{RT}\right) [\text{OH}]^{0.70} P_{\text{O}_2}^{0.74} K^{3.07} u(t-2) \quad (6)$$

$$-\frac{d[\text{OH}]}{dt} = \frac{F_{\text{alkali, solution}} ([\text{OH}] - [\text{OH}])}{V} - 5 \cdot \Delta K + [\text{OH}] \quad (7)$$

$$-\frac{d[\text{OH}]}{dt} = \frac{F_{\text{alkali, solution}}([\text{OH}] - [\text{OH}])}{V} - 8 \cdot \Delta K + [\text{OH}] \quad (8)$$

Where Eq. 7 represents alkali consumption for the first 2 min and Eq. 8 represents the alkali consumption for the rest of the reaction time.

Differences between the predicted and the actual kappa number did not exceed 8.4%, which is comparable to the error values found in the literature. The alkali concentration was not available, so we had to use average values.

The results using Model 2, which is based on Agarwal's model, were worse than the ones obtained with Model 1. Once again, the parameters were adjusted using GA and the reaction orders were kept as proposed by the authors. Agarwal et al. used a higher reaction order on the kappa number, so we applied Schön's model to improve their results.

In a tentative of improvement of Model 2, the reaction order on the kappa number was varied with the other parameters. The value obtained for the reaction order on the kappa number is very similar to the equivalent reaction order of the other models. This result showed that, for this particular process, the reaction order on the kappa number must be set on the interval [3, 4]. The resulting kinetic equations for Model 2 are:

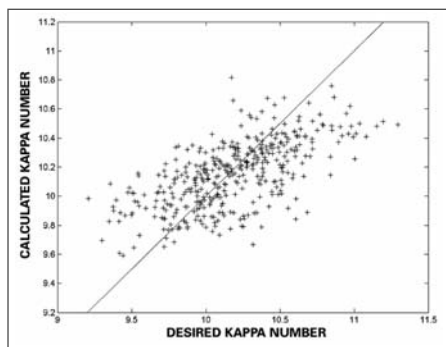
$$-\frac{dk}{dt} = 1,3 \times 10^{-2} \exp\left(-\frac{3,8 \times 10^4}{RT}\right) [\text{OH}]^{0,92} P_{\text{O}_2}^{0,53} K^{3,37} \quad (9)$$

$$-\frac{d[\text{OH}]}{dt} = \frac{F_{\text{alkali, solution}}([\text{OH}] - [\text{OH}])}{V} - 6 \cdot \Delta K + [\text{OH}] \quad (10)$$

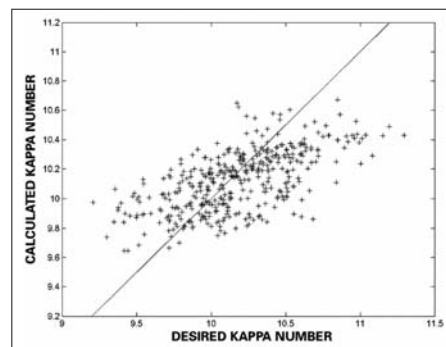
The predicted kappa number presents a slight difference from the actual pulp kappa number (Fig. 4). However, the values used for alkali concentration are not as accurate as desirable for modeling. Relative errors are around 8.3%, which means that Models 1 and 2 are equivalent.

For Violette's model (from now on referred as Model 3), GA adjustment was applied to vary activation energy, Arrhenius frequency factor, and the alkali consumption kinetic parameter. Figure 5 shows the results obtained; the resulting kinetic equations are:

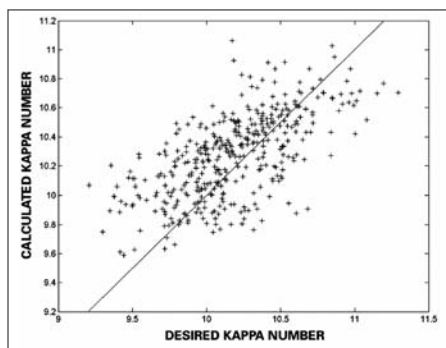
$$-\frac{dk}{dt} = 11,6 \times 10^3 \exp\left(-\frac{7,2 \times 10^4}{RT}\right) [\text{OH}]^{0,588} K^{3,12} \quad (11)$$



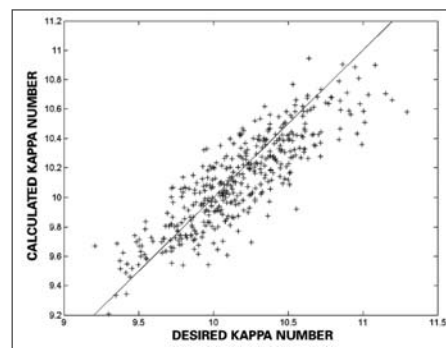
3. Comparison between kinetic model 1 results and the actual delignification plant outlet kappa number.



4. Comparison between kinetic model 2 results and the actual delignification plant outlet kappa number.



5. Comparison between kinetic model 3 results and the actual delignification plant outlet kappa number.



6. Comparison between neural network output and the actual delignification plant outlet kappa number.

$$-\frac{d[\text{OH}]}{dt} = \frac{F_{\text{alkali, solution}}([\text{OH}] - [\text{OH}])}{V} - 6 \cdot \Delta K + [\text{OH}] \quad (12)$$

Model 3 presents a predictive quality comparable to the other two models. The benefit of this adjustment is its possible use to indicate excess oxygen in the reactor. Relative errors are around 9.3%, which is not significantly higher than the Model 1 and 2 errors. Model 3 can also be improved with more accurate alkali concentration values, but further investigation is necessary to confirm oxygen excess.

All three models provide kappa number and alkali consumption profiles. These profiles are useful to analyze the reaction quality, making it possible to evaluate alkali excess and to identify the first stage of delignification, where there is a sharp decrease in the delignification rate.

When it comes to the neural network model, several network architectures were tested. We varied the number of neurons on the hidden layers and tried

different combinations of inputs. The final network structure consists of five neurons in the hidden layer and five inputs (inlet kappa number, temperature, oxygen and alkali flow, and pulp production). The results obtained are logically better, with relative errors around 6.3%. This result was expected; neural networks are prepared to learn the process and to reproduce it accurately. Figure 6 presents a comparison between the predicted and the actual kappa number.

Concluding Remarks

Both models—kinetic and neural network—produced similar results, with relative errors on the same order of magnitude. These results indicate that the neural networks can be used for simulation and for process optimization when the system is partially known. It can be developed using only process variables and therefore does not require previous knowledge of kinetic or mass transfer parameters.

On the other hand, kinetic models provide a better process interpretation and they are valid for a wider range of

PROCESS SIMULATION

operational variables, while the neural network is accurate only in the training region.

All of the presented models offer the benefit of a simulation program, assisting decision making on process policies according to the desired product characteristics. The models enable mill personnel to correct the process before undesired pulp grades are produced. It can also be a useful tool for operators and engineers training. **TJ**

NOMENCLATURE

K = kappa number

t = time, min

k = kinetic constants

E_a = activation energy, kJ/kmol

R = gas constant, 8314 kJ/kmol•K

T = temperature, °C for Model 1 and K for Models 2 and 3

$[OH]$ = alkali concentration, kol/m³ for Model 1 and g/L for Models 2 and 3

P_{O_2} = oxygen partial pressure, kPa

$F_{alkali\ solution}$ = alkali solution flow, L/min

V = reactor volume, for Model 1 and for Models 2 and 3

d = Alkali consumption kinetic parameter

ΔK = kappa number variation.

Subscripts are

1,2 = first and second reaction stages, respectively

i = initial condition.

LITERATURE CITED

1. Hsu, C.L. and Hsieh, J.S., *AIChE Journal*, 34(1):116(1988).
2. Hsu, C.L. and Hsieh, J.S., *Tappi J*, 68(6): 92(1985).
3. Agarwal, S.B., Genco, J.M., Cole, B.J.W., et al. *J. Pulp Paper Sci.*, 25(10): 361(1999).
4. Violette, S.M., "Oxygen delignification kinetics and selectivity improvement," PhD Thesis. University of Maine (2003).
5. Olm, L. and Teder, A., *Tappi* 62(12): 43(1979).
6. Olm, L. and Teder, A., *Paperi Puu*, 63(4a): 315(1981).
7. Myers, M.R. and Edwards, L.L., *Tappi J*. 72(9): 215(1989).
8. Yamamoto, C.I. "Modelagem matemática e otimização do processo industrial de síntese de amônio utilizando redes neurais," PhD Thesis. Escola Politécnica de São Paulo (1998).
9. Haykin, S., *Neural Network*. 2nd ed. Porto Alegre: Bookman, 2001.
10. Meleiro, L.A., "Projeto e Aplicação de Controladores Baseados em Modelos Lineares, Neurais e Nebulosos," PhD Thesis. Universidade Estadual de Campinas (2002).
11. Aguiar, H.C.I.L. and Maciel Filho, R. *Comp. Chem. Eng.* 22(Suppl):S981 (1998).
12. Schöön, N-H., *Svensk Papperstidning*, R185-R-193, 1982.

Received: December 16, 2005

Accepted: February 6, 2006

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the May *Solutions! for People, Processes and Paper* magazine (Vol. 89 No. 5).

INSIGHTS FROM THE AUTHORS

We first became interested in cellulose and paper research in 2004 when we started to develop kinetic and neural network models for this research field. We've been working with models since 2002; working with cellulose opened a new research area for us.

During our current research, our main difficulty was data acquisition, since the mill was 300 km (more than 180 miles) away from our research laboratory. We had to be very careful during data collection to avoid having to make several trips.

During this research, we discovered that we really enjoyed working with cellulose—we are now developing new projects in this field. That was the most surprising thing for us. We were used to working with models for any process, and now we're devoted to delignification and bleaching research.

Overall, we feel that models are very useful for mills. From mill personnel training to savings of reactants, this work presents options for how the results can be used. The next step is the bleaching plant—that is, to model the bleaching stages kinetically and with other techniques.

Rubini is with Universidade Federal do Paraná – PIPE – Programa de Pós-Graduação em Engenharia Curitiba, PR, Brasil, CX Postal: 19011 - CEP: 81531-990. Yamamoto is a professor at the Chemical Engineering Department, Universidade Federal do Paraná—PR, Brasil. Email Rubini at bibianaoui@yahoo.com and Yamamoto at ciyama@ufpr.br.



Yamamoto



Rubini