Modeling and Dynamic Simulation of a Bleach Plant

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A dynamic model of five-stage (C+D)EDED bleach plant was developed using SIMNON, a dynamic simulation language developed at Lund Institute of Technology, as a platform. The model is composed of individual modules that represent each bleaching stage. Each module includes chemical addition and mixing, diffusion and reaction in a retention tower, and washing. These unit operations are coupled with chemical kinetics for each bleaching stage using appropriate models. A relationship between the (C+D)E Kappa number and the input absorption coefficient to the D_1 stage was used to link the delignification and brightening partial sequences of the bleach plant. The model, verified using steady-state data, was used to model the dynamic response of the plant to step changes in production rate, (C+D) chemical addition, and incoming Kappa number, as well as the open-loop response of the plant to a simulated variation in incoming Kappa number. The modular structure of the program allows a variety of bleach plants to be assessed once flow parameters and chemical kinetics are known. The dynamic model can also be used to develop and compare control strategies before being implemented at the mill.

Introduction

In pulp bleaching, sequences of chemicals are used to increase pulp brightness by removing or modifying the color-producing lignin that remains in the fibers after cooking. Recently, bleach plants have come under intense scrutiny due to increased environmental awareness. New bleaching sequences have been proposed to eliminate the use of chlorine-based chemicals, while increased system closure is being examined to minimize water usage and reduce the volume of effluent requiring treatment.

Steady-state simulators like GEMS (Edwards et al., 1983), MASSBAL (1983), MAPPS (1984) and PAPMOD (1988) can be used for the design of these systems. However, true dynamic simulators are needed to assess the performance of bleaching sequences because of their complex dynamics, particularly in the design of new control strategies (Roche and Bouchard, 1982). Dynamic versions of existing steady-state simulators such as GEMS, MASSBAL and PAPMOD have emerged in the past few years along with general dynamic simulation packages such as SIMULINK, MODEL-C, SIMUSOLV, EXTEND, DTISS, ACSL, and SIMNON. Each package has its advantages and disadvantages, and should be chosen depending on the type of applications.

A number of investigators have studied the dynamic behavior of various parts of the bleach plant. Mackinnon (1987) developed a FORTRAN simulation program for the first chlorination and second alkaline extraction stages. Kinetic expressions of the chlorination and oxidative extraction were derived to match experimental data and the simulation was used to compare operation strategies. Bialkowsky (1990) used first-order plus dead-time transfer functions to represent the dynamics of bleaching systems. The model was used to review control engineering principles and how bleach plant process variability can be minimized. Ulinder (1992) used the Simon's IDEAS simulation package to model the oxygen bleaching stage. The model was used to test an advanced Kappa number control scheme.

In the present study, a detailed dynamic simulation for a bleach plant is presented. SIMNON (1991) was chosen as the simulation platform because of its modular feature and a RK4 algorithm for solving ordinary differential equations. A FORTRAN subroutine was written and linked to SIMNON to solve the partial differential equations based on the work of

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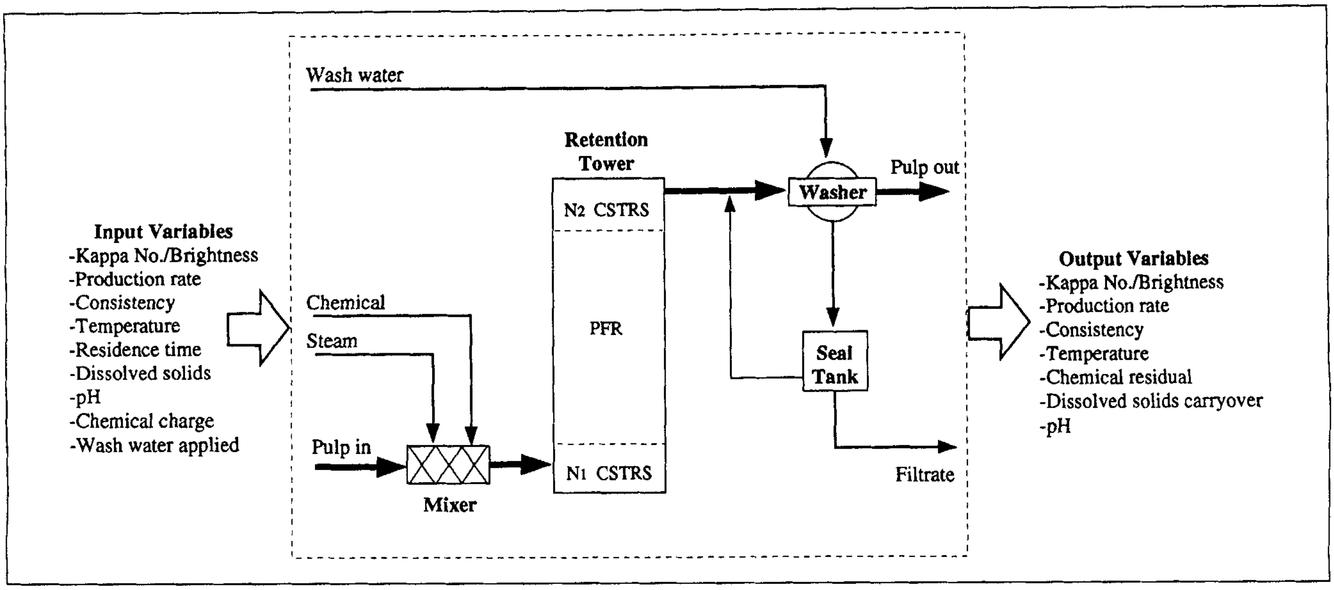

Figure 1. Process units and variables of a bleach stage.

The parameters required to model each stage in a (C + D)EDED bleach plant are given in Table 2.

Patankar (1980). Mathematical models were developed for each pulp processing unit and linked together to create a generic bleaching stage. The inclusion of appropriate chemical kinetics allowed modeling of any specific stage. The individual stages can then be linked, as required, to model a complete bleach plant. A (C + D)EDED plant was chosen for the simulation presented here due to its wide use in industry and the availability of good chemical kinetic models for the bleaching reactions. The model was used to study the dynamic response of brightness and chemical residual to changes in production rate, chemical charge, and incoming Kappa number. The effect of the frequency content of a typical disturbance was simulated to examine its impact on bleach plant operation. The bleach plant model can be adapted to simulate other or newer bleaching sequences provided kinetic models for the bleaching reactions are available.

Process Description

Bleaching is carried out in a continuous sequence of distinct stages. Each stage uses a combination of mixing, reaction, and washing steps that require distinct pieces of process equipment: (1) mixers to achieve a uniform contact between fibers and bleaching chemicals and/or steam; (2) retention towers to permit diffusion and completion of the chemical reactions; and (3) washers to separate the pulp from the spent bleaching chemicals and the material dissolved during the bleach stage. Filtrate from each washer is recycled within the stage for dilution of the pulp suspension and may be delivered to previous stages for washing in a number of countercurrent washing schemes. Optimization of each bleach stage must be achieved and requires control of chemical addition, pH, temperature and residence time. The process units and key variables of a bleaching stage are shown in Figure 1.

The (C + D)EDED bleaching sequence we model uses chlorine and chlorine dioxide in the (C + D) stage followed by an alkaline extraction using sodium hydroxide in the E stage. This partial sequence concentrates on lignin removal. Chlorine dioxide can be applied at a low percentage (on the order of about 10%) to protect pulp strength or at higher percentages (up to 100%) for dioxin reduction and AOX minimization. The DED partial sequence develops pulp brightness using chlorine dioxide and sodium hydroxide. A flowsheet of a typical (C + D)EDED bleach plant is shown in Figure 2. Additional details on bleaching processes can be found in a number of reference texts, including Singh (1979) and Patrick (1991).

Model Development

The mathematical model of a multistage bleach plant must be capable of addressing interactions between important process variables within and between each bleaching stage. This is accomplished by identifying the most important chemical and physical phenomena and including them in the model.

In a (C + D)EDED bleach plant, the Kappa number after the E_1 stage measures the degree of delignification and is an important control target. The brightness after the D_1 and D_2 stages are important control targets for DED brightening. Thus, to model the complete bleaching sequence, it is necessary to relate the Kappa number leaving the E_1 stage to the brightness entering the D_1 stage. This is accomplished by correlating the E_1 Kappa number with the light absorption coefficient after (C + D)E bleaching.

In each stage, the bleaching reactions are modeled by reaction kinetics that lump mass-transfer and chemical reactions together. These reactions take place both in the mixer and in the subsequent retention tower. The dynamics of the retention towers play the dominant role in the transient behavior of a bleaching stage due to its long residence time (30 to 240 min, depending on the chemistry) compared with the other process operations. Indeed, tower residence time accounts for

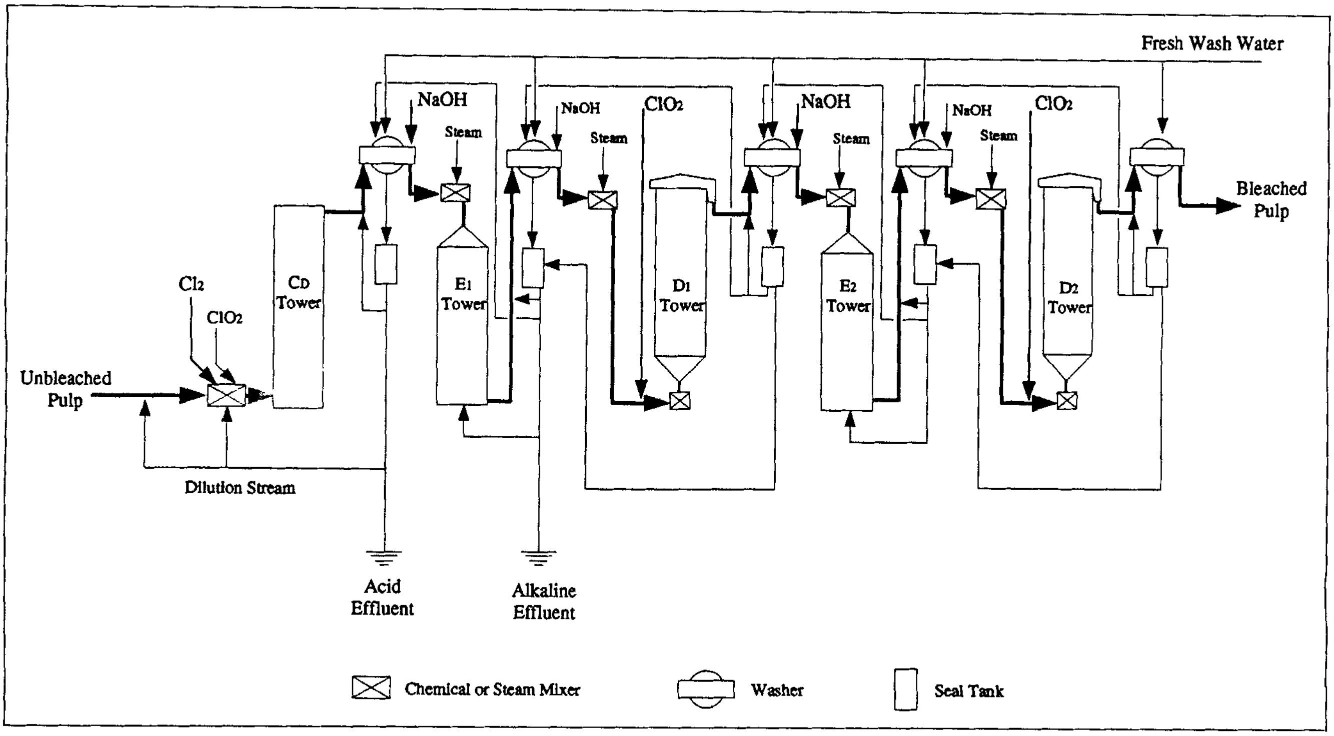

Figure 2. Process flow diagram of a typical (C + D)EDED bleach plant with a direct countercurrent washing scheme.

over 98% the total residence time in a bleach plant (Mackinnon, 1987) and thus must be modeled accurately.

Models for bleaching unit operations

Mathematical models for mixing, retention, and washing were formulated and incorporated into the SIMNON framework. The addition of appropriate reaction kinetics into these modules permit modeling of particular bleaching stage and are described later.

Mixer. The mixing module describes the addition of chemicals, steam, or recycled liquor to the pulp suspension and calculates the initial concentrations for the bleaching reaction. The mixing module has two or more inlet streams and one exit stream. The outputs from the mixing module are used as inputs for the retention tower, as shown in Figure 1. We assumed perfect mixing and steady-state operation for the mixer which permits the following equations for the components in exiting stream to be written.

For the liquor:

$$L_o = L_i + V_i \tag{1}$$

For the fibers:

$$C_{mo} = \frac{L_i \cdot C_{mi}}{L_o \cdot (1 - C_{mi}) + L_i \cdot C_{mi}} \tag{2}$$

For the chromophores (expressed as Kappa number and light absorption coefficient):

$$K_o = K_i \tag{3}$$

For chemical and dissolved solids:

$$X_{j,o} = \frac{L_i \cdot X_{j,i} + V_i \cdot Y_{j,i}}{L_o} \tag{4}$$

where j refers to the species in the liquor stream (Cl_2, ClO_2, H^+, OH^- and dissolved solids).

Retention tower

Past simulations have used a plug-flow model for their simulations (Ackert et al., 1975; Mackinnon, 1987; Myers and Edwards, 1989; Ulinder, 1992) giving only a pure time delay response not found in industrial bleach plants (Snyder, 1966; Perkins, 1971). Here, deviations from plug flow are caused by a number of factors, including channeling, axial mixing, and radial variations in flow velocity. Mixing also occurs at the top and bottom of the towers due to the presence of impellers and/or rakes in these sections. For controller design, first-order plus delay transfer functions have also been used to characterize dynamics of the key process variables, such as consistency, Kappa number, and brightness (Bialkowsky, 1990). This type of approach assumes that the system is linear, which is not the case in practice.

The flow behavior in a bleaching tower can be approximated by a number of models (Levenspiel, 1972). We examined three here. The first model, CSTR, uses a number of continuous stirred tank reactors in series to model the response measured for the tower. The second model, CSTR + PFR, uses a single CSTR followed by a plug-flow reactor to model the flow. The third model, CSTRS-PFR-CSTRS, com-

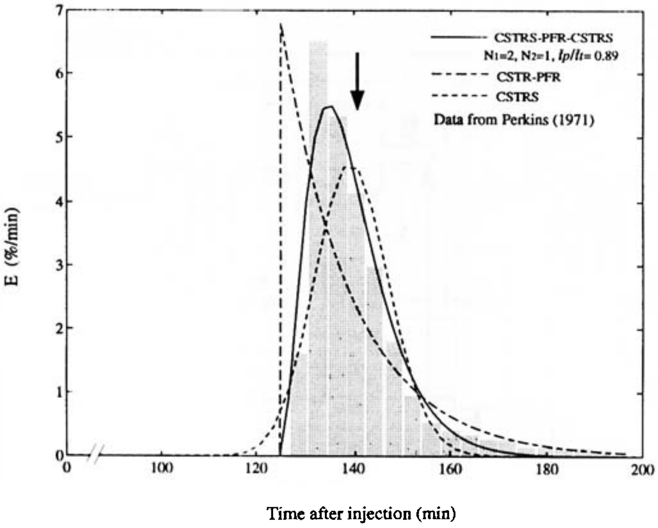

Figure 3. Measured residence time distribution and model predictions for an upflow D_2 tower.

bines a number of CSTRs before and after a plug-flow reactor. In this latter case, the number of CSTRs and the PFR residence time can be varied to model a range of tower responses. The model is close to the picture we have of a typical bleaching tower and gives the best agreement with experimental retention time distributions, as shown in Figure 3. Other examples have been presented previously (Wang et al., 1994).

The flow parameters for the CSTRS-PFR-CSTRS model were determined by fitting the model with available tracer data in the literature (Snyder, 1966; Perkins, 1971). The model must have the same mean residence time and variance as the experimental E-curve. The percentage of the residence time taken by plug flow was found to vary from 79 to 85% for C towers and 82–90% for E and D towers. The numbers of CSTRs used to represent the mixing that occurs at the bottom and top of tower (N1 and N2) are given in Table 1 for each stage.

The CSTR is used to represent the mixing regions in retention towers and process mixers. We assume a constant liquor density and write:

For liquor:

$$L_o = L_i \tag{5}$$

For fibers:

$$\frac{dC_{mo}}{dt} = \frac{C_{mi} - C_{mo}}{\bar{t}_c} \tag{6}$$

For chromophores:

$$\frac{dK_o}{dt} = \frac{C_{mi} \cdot (K_i - K_o)}{\bar{t}_c \cdot C_{mo}} - r \tag{7}$$

For each component in the liquor:

$$\frac{dX_{j,o}}{dt} = \frac{X_{j,i} - X_{j,o}}{\bar{t}_c} - \frac{C_{mo}}{1 - C_{mo}} \cdot \Psi_j \cdot r \tag{8}$$

where $j = Cl_2$, ClO_2, H^+, OH^- and dissolved solids. Here, $\bar{t}_c$ is the mean residence time of the CSTR, r is the rate of chromophore removal (Kappa number or light absorption decrease), and the product, $C_{mo}/(1 - C_{mo}) \cdot \Psi_j \cdot r$, is the reaction rate for the bleaching liquor components. The stoichio-

Table 1. Input Data for Simulation of (C + D)EDED Bleach Plant

Stage	C+D	E	D	E	D
Cl_2					
Flow, kg/min	19.5	-	-	-	-
Conc., %	100	-	-	-	-
ClO_2					
Flow, kg/min	8.2	-	26	-	13
Conc., %	10	-	10	-	10
NaOH					
Flow, kg/min	-	137	22	31	3
Conc., %	-	7	7	7	7
Steam, kg/min	-	581	581	581	581
Tower					
ρ_1, kg/m^3	1,000	1,000	1,000	1,000	1,000
Temp, °C	40	70	70	70	70
Consistency, %	3.0	10.0	6.0	10.0	6.0
$\bar{t}_t$, min	40	60	120	60	120
$\bar{t}_p/\bar{t}_t$	0.80	0.90	0.90	0.90	0.90
N_1	1	2	2	2	2
N_2	1	1	1	1	1
Kinetics			See **Kinetic Models**		
Washer					
E_N	3.0	3.0	3.0	3.0	3.0
Wash liquor, kg/min	3,696	5,934	3,696	6,099	3,696
Outlet consist., %	12	8.0	12	7.8	12
Unbleached pulp	Pulp flow rate = 14,351 kg/min, Consistency = 3% Kappa No. = 25.2, Dissolved solids content = 0.2 %, pH = 7				

metric coefficient Ψ_j is positive for reactants: Cl_2, ClO_2 and OH^-, and negative for the products: H^+ and DS. Reaction rate expressions are added for each stage as described later. The stoichiometric relationship for dissolved solids is determined from the amount of lignin dissolved in each bleaching stage.

The PFR models the plug-flow region of the retention tower. For a constant liquor density, the mass balance for liquor becomes:

$$L_o = L_i \tag{9}$$

For fibers:

$$\frac{\partial C_m}{\partial t} = -\frac{\partial C_m}{\partial \bar{t}} \tag{10}$$

For chromophores:

$$\frac{\partial K}{\partial t} = -\frac{\partial K}{\partial \bar{t}} - r \tag{11}$$

For each component in liquor:

$$\frac{\partial X_j}{\partial t} = -\frac{\partial X_j}{\partial \bar{t}} - \left(\frac{C_m}{1-C_m}\right)\cdot\Psi_j\cdot r \tag{12}$$

Washer

Each drum washer is composed of three major components: the dilution vat, drum filter, and seal tank. The dilution vat is modeled as a steady-state mixer. The drum filter can be described using the displacement ratio (Perkins, 1954) or the Norden efficiency (Norden, 1966, 1987), and the seal tank can be represented as a continuous stirred tank (Perron and Lebeau, 1977; Näse and Sjöberg, 1989; Turner et al., 1990). We have chosen the following model for bleaching plant washers (Wang, 1993):

Dilution vat:

$$L_v = L_i + V_r \tag{13}$$

$$X_{DS,v} = \frac{L_i\cdot X_{DS,i} + V_r\cdot Y_{DS,o}}{L_v} \tag{14}$$

Drum filter:

$$L_1 = L_0\cdot\frac{C_{m0}}{1-C_{m0}}\cdot\frac{1-C_{m1}}{C_{m1}} \tag{15}$$

$$X_{DS,1} = \begin{cases} Y_{DS,2} + \dfrac{RW-1}{RW^{E_N}\cdot V_d/L_v - 1}\cdot(X_{DS,v} - Y_{DS,2}) \\ \text{when} \quad RW \neq 1 \\ Y_{DS,2} + \dfrac{1}{E_N}\cdot(X_{DS,v} - Y_{DS,2}) \\ \text{when} \quad RW = 1 \end{cases} \tag{16}$$

$$V_d = V_2 + L_v - L_1 \tag{17}$$

$$Y_{DS,d} = \frac{V_2\cdot Y_{DS,2} + L_v\cdot X_{DS,v} - L_1\cdot X_{DS,1}}{V_d} \tag{18}$$

Seal tank:

$$\frac{dH_{st}}{dt} = \frac{(V_d - V_1 - V_r)}{V_{st}\cdot\rho_l} \tag{19}$$

$$\frac{dY_{DS,1}}{dt} = \frac{V_d\cdot(Y_{DS,d} - Y_{DS,1})}{V_{st}\cdot H_{st}\cdot\rho_l} \tag{20}$$

Kinetic models

The most important aspect in modeling a pulp bleaching process is knowledge of the reaction kinetics. Kinetic models available in the literature for (C + D), E and D bleaching were used (Ackert et al., 1973; Axegård, 1979; Teder and Tormund, 1977, 1980; Axegård and Teder, 1984). The removal of chromophores in pulp is characterized by a decrease in Kappa number in the delignification partial sequence and by a decrease in the light absorption coefficient in the brightening stages.

Chlorine delignification

Of the kinetic models proposed for chlorine bleaching (Chapnerkar, 1961; Russel, 1966; Karter, 1968; Ackert, 1973; Mackinnon, 1987; Germgård and Karlsson, 1985), the model by Ackert et al. (1973) is chosen for its simplicity and accuracy. This model divides the lignin entering the (C + D) stage into three types: fast reacting, slow reacting, and a floor level or unreactive lignin. The rate of the fast lignin removal is given by:

$$r_{C,f} = -\frac{dK_{C,f}}{dt} = k_{C,f}\cdot[Cl_2]\cdot K_{C,f} \tag{21}$$

while the rate of the slow lignin removal is

$$r_{C,s} = -\frac{dK_{C,s}}{dt} = k_{C,s}\cdot[Cl_2]\cdot K_{C,s} \tag{22}$$

where the reaction rate constants, $k_{C,f}$ and $k_{C,s}$, are expressed as

$$\begin{aligned} k_{C,f} &= 1{,}123\cdot\exp\left(\frac{-250}{T}\right) \\ k_{C,s} &= 22.47\cdot\exp\left(\frac{-250}{T}\right) \end{aligned} \tag{23}$$

with $[Cl_2]$ being the concentration of chlorine (mol/L), and $K_{C,f}$ and $K_{C,s}$, the content of the fast and slow lignin each, expressed as the Kappa number. (k rate constant of bleaching reactions and units, vary with different reaction orders.)

The total Kappa number is then:

$$K_C = K_{C,f} + K_{C,s} + K_{C,\infty} \tag{24}$$

where $K_{C,\infty}$ is the floor level or unreactive lignin.

The initial values of the fast and slow Kappa numbers $K_{C,f,o}$ and $K_{C,s,o}$ are given by:

$$\begin{aligned} K_{C,f,0} &= 0.5 \cdot K_{C,0} \\ K_{C,s,0} &= 0.3 \cdot K_{C,0} \end{aligned} \tag{25}$$

where $K_{C,0}$ is Kappa number of the unbleached pulp.

The stoichiometric relationship between chlorine consumption and decrease in Kappa number is:

$$\frac{\text{Cl}_2 \text{ consumption (\% on od pulp)}}{\text{Kappa number decrease}} = \Psi_{\text{Cl}_2} \tag{26}$$

where Ψ_{Cl_2} is the stoichiometric coefficient with a value of 0.208 (Karter, 1968).

The kinetics of chlorine bleaching with low chlorine dioxide substitution are assumed to be the same as with chlorine bleaching. In this case, we express the chlorine charges as total equivalent chlorine, including chlorine dioxide, with 1 kg of ClO_2 equivalent to 2.63 kg of chlorine.

First alkaline extraction

The reaction kinetics and lignin solubilization mechanism during the first extraction stage are poorly understood. This lack of understanding is reflected by the fact that only three attempts at modeling extraction kinetics have been published (Axegård, 1979; Mackinnon, 1987; Taylor et al., 1982). In the present study, we have developed a model based on Axegård's approach.

Axegård's model represents the extraction of chlorine bleached pulp by two parallel first-order reactions with respect to the Kappa number decrease: one is the extraction of fast lignin and the other is the extraction of slow lignin. Here, the fast and slow lignin for the extraction are different from those in the chlorination, with the initial ratio of the fast ($K_{E_1,f}$) and slow ($K_{E_1,s}$) Kappa numbers given as a function of the initial alkalinity, chlorine charge, and temperature.

$$\frac{K_{E_1,f,0}}{K_{E_1,s,0}} = 1.75 \times 10^5 \exp\left(\frac{-3{,}368}{T}\right) \cdot [\text{OH}^-]^{0.25} \cdot f \tag{27}$$

Here $K_{E_1,f,0} + \text{K}_{E_1,s,0} = K_{E_1,0}$ is the initial Kappa number of the extraction reaction as calculated from the chlorination stage (K_c after (C+D) bleaching), and f is the chlorine charge factor (% active Cl_2 on od pulp/unbleached Kappa number).

The rate of the two extraction reactions is expressed as follows:

$$\begin{aligned} r_{E_1,f} &= -\frac{dK_{E_1,f}}{dt} = k_{E_1,f} \cdot [\text{OH}^-]^{0.2} K_{E_1,f} \\ r_{E_1,s} &= -\frac{dk_{E_1,s}}{dt} = k_{E_1,s} \cdot [\text{OH}^-]^{0.05} \cdot K_{E_1,s} \end{aligned} \tag{28}$$

where $[\text{OH}^-]$ is hydroxyl ion concentration (mol/L). The rate constants of the fast and slow reactions, $k_{E_1,f}$ and $k_{E_1,s}$, depend on the reaction temperature as follows:

$$\begin{aligned} k_{E_1,f} &= 1.96 \times 10^6 \cdot \exp\left(\frac{-4{,}691}{T}\right) \\ k_{E_1,s} &= 0.0103 \cdot \exp\left(\frac{-241}{T}\right) \end{aligned} \tag{29}$$

Axegård's model indicates that the hydroxide concentration has a very slight effect on both the fast and slow reactions (Eq. 28) while higher initial alkalinity results in a larger proportion of fast lignin (Eq. 27). Although the alkali concentration decreases during extraction in practice, it was found that the Kappa number could be satisfactorily predicted using the initial alkali concentration.

We tested Axegård's model with experimental data at different chlorine charges and found that the model fitted the data quite well for an active chlorine charge of 0.25. However, as the chlorine charge factor was lowered, the model underpredicted the Kappa numbers measured experimentally. This discrepancy increased as the chlorine charge decreased. Axegård's model assumed that the intensity of chlorination influenced only the initial distribution between the fast and slow Kappa numbers instead of the reaction rates (Eqs. 27 and 29). A more reasonable implication for the effect of chlorination intensity is that the rate of lignin solubilization depends also on the chlorine charge in the previous stage. Our model assumes that the reaction constants are proportional to the chlorine charge factor and the ratio of initial Kappa numbers is independent of chlorination intensity. By fitting the experimental data, new reaction constants were determined:

$$\begin{aligned} k_{E_1,f} &= 9.78 \times 10^6 \cdot \exp\left(\frac{-4{,}691}{T}\right) \cdot f \\ k_{E_1,s} &= 0.0515 \cdot \exp\left(\frac{-241}{T}\right) \cdot f \end{aligned} \tag{30}$$

with the ratio of initial Kappa numbers given as

$$\frac{K_{E_1,f,0}}{K_{E_1,s,0}} = 2.72 \times 10^4 \cdot \exp\left(\frac{-3{,}368}{T}\right) \cdot [\text{OH}^-]^{0.25} \tag{31}$$

Figure 4 gives a comparison between our model and Axegård's model for the alkaline extraction of a number of chlorinated pulps. Our model represents the experimental data better than Axegård's model when the chlorine charge factor is below 0.2. We found our model had a normalized standard deviation of 0.6% compared with 0.8% for Axegård's model. Table 2 shows a comparison using the experimental results of Histed et al. (1985), which were obtained over a much wider range of chlorine charges. This suggests that our description of the dependence on chlorination intensity is more suitable over a wider range of chlorine charges.

Axegård's and our model were also compared for extraction of a chlorine dioxide bleached pulp using data from Axegård (1979), as shown in Figure 5. Good agreement was ob-

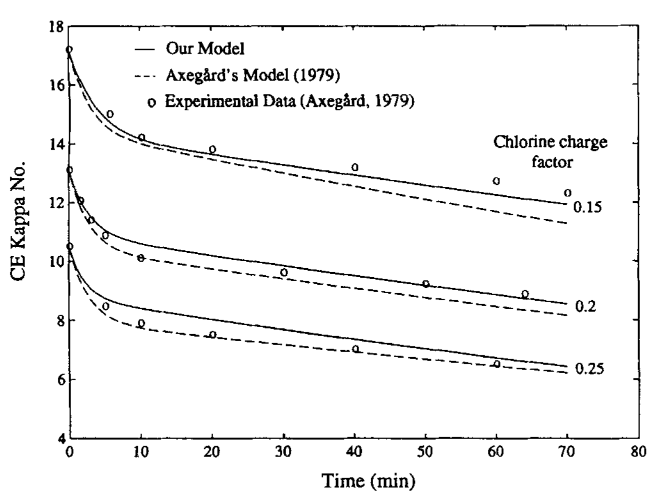

Figure 4. Kappa number during CE bleaching.

tained using our model by replacing values of the coefficients in Eq. 30 (9.78×10^6 becomes 6.85×10^6 for extraction of ClO_2 bleached pulp and 0.0515 becomes 0.0165). The other model parameters remain the same. The reaction mechanisms and factors governing the delignification rate seem to be the same for extraction of both chlorine and chlorine dioxide bleached pulps over the range examined.

First chlorine dioxide bleaching

The kinetic model of Teder and Tormund (1977, 1980) is used for the D_1 stage. Here:

$$r_{D_1} = -\frac{dK_{D_1}}{dt} = k_{D_1}\cdot[ClO_2]^{0.5}\cdot[H^+]^{-0.3}\cdot(K_{D_1}-K_{D_1,\infty})^3 \qquad (32)$$

with

$$k_{D_1} = A_1\cdot\left(\frac{1}{K^2_{D_1,0}}+A_2\right)\cdot\exp\left(\frac{-E_a}{R\cdot T}\right) \qquad (33)$$

where K_{D_1} is the chromophore content of the pulp expressed as the light absorption coefficient at 457 nm, $K_{D_1,\infty}$ is the floor light absorption coefficient (~0.1 m^2/kg), $[ClO_2]$ is the molar concentration of ClO_2, $[H^+]$ is the molar concentration of H^+, E_a is the activation energy (~59 kJ/mol), and $K_{D_1,0}$ is the initial light absorption coefficient. The constants A_1 and A_2 are dependent on the type of prebleaching. $A_1 = 0.145\times10^{10}$ and $A_2 = -0.435\times10^{-3}$ are the values published for (C+D)E prebleached pulp (Teder and Tormund, 1980).

Table 2. Our Model vs. Axegård's Model (from Histed et al., 1985)

		CE Kappa No.		
Cl_2 Charge Factor	C Kappa No.	Exp.	Pred. by Modified Model	Pred. by Axegård
0.16	16.1	6.1	6.1	5.7
0.2	13.0	4.8	4.7	4.1
0.22	10.5	3.7	3.7	3.1
0.26	7.7	3.0	2.6	2.1
0.29	6.0	2.6	1.9	1.5
0.32	5.0	1.9	1.5	1.2

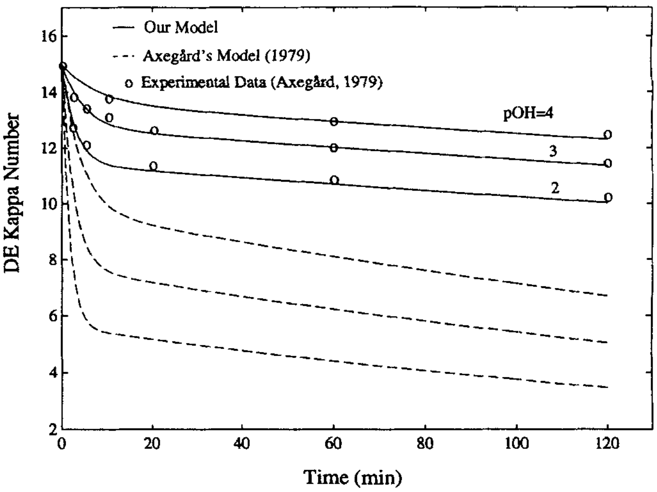

Figure 5. Kappa number during DE bleaching.

The stoichiometric relationship for ClO_2 consumption is:

$$\frac{ClO_2\text{ consumption (\% on od pulp)}}{\text{Light absorption coefficient decrease}} = A_3\cdot\frac{1}{K^n_{D_1}} = \Psi_{ClO_2} \qquad (34)$$

where $A_3 = 0.292$ and $n = 1.0$ (Teder and Tormund, 1980).

The stoichiometric equation for H^+ generation is:

$$\frac{H^+\text{ generation (\% on od pulp)}}{\text{Light absorption coefficient decrease}} = \Psi_{H^+} \qquad (35)$$

where Ψ_{H^+} was found to be directly proportional to Ψ_{ClO_2} and independent of pH, pulp type and temperature (Teder and Tormund, 1980).

Second alkaline extraction and second chlorine dioxide bleaching

The E_2 stage itself cannot delignify or brighten pulp (Axegård and Teder, 1984). The main effect of the E_2 stage is to improve the reactivity of the fibers by swelling them and to decrease the ClO_2 consumption in the subsequent D_2 stage. The bleaching efficiency of the D_2 stage can be increased by increasing the alkalinity, temperature, or reaction time in the E_2 stage. Therefore, the kinetic model for the D_2 stage should incorporate the influencing factors of the E_2 stage. As suggested by Axegård and Teder, D_2 bleaching can be described by the same kinetic model used for the D_1 stage (Eqs. 32 to 35) with the following modifications. New values are required for A_1 and n, with $A_1 = 0.117\times10^9$ and $n = 2.5$. A_2 and A_3 are expressed as functions of the conditions in the E_2 stage:

$$A_2 = B_1\cdot[OH^-]^{0.1}\cdot t_r^{0.3}\cdot\exp\left(\frac{-E_{a1}}{R\cdot T}\right) \qquad (36)$$

and

$$A_3 = B_2 \cdot [\mathrm{OH}^-]^{-0.08} \cdot \exp\left(\frac{-E_{a2}}{R \cdot T}\right) \qquad (37)$$

Here $[\mathrm{OH}^-]$, t_r, and T are the alkalinity, retention time, and temperature of the E_2 stage. The constants B_1 and B_2 in Eqs. 36 and 37 were estimated to be 9.1×10^{12} and 0.02 by fitting the model to experimental data. $E_{a1} = 15$ kJ/mol and $E_{a2} = -8$ kJ/mol were given by Axegård and Teder (1984). The authors found that higher E_1-stage temperatures resulted in lower ClO_2 consumption in the D_2 stage, and thus a negative value was given for E_{a2}.

Correlation of light absorption coefficient with Kappa number after the E_1 stage

In order to simulate the whole bleach plant it is necessary to link the delignifying (C + D)E partial sequence with the DED brightening sequence. This was done by developing a correlation between the Kappa number after the E_1 stage and the light absorption coefficient entering the D_1 stage.

The Kappa number is measured using a standard chemical method (CPPA, 1984) which gives the lignin content of the pulp by titration of chemicals groups which have been oxidized. We have assumed as a first approximation that it is related to the chromophore concentration. The light absorption coefficient is an optical measurement which measures the chromophore content of the pulp during the brightening phase (Norrström, 1972). Norrström has shown that a theoretical relationship exists between the absorption coefficient of pulp and the content of the chemical species responsible for pulp color. However, there is no quantitative correlation between initial light absorption coefficient and lignin content or Kappa number given in the literature. We therefore developed such a relationship in order to link the delignification and brightening sequences in the bleach plant. Our model is derived from Norrström's theory (1972) that the light absorption coefficient of pulp is directly proportional to the content of chromophores in the pulp:

$$K = \sum_j K_j \cdot C_j \qquad (38)$$

where C_j is the content of chromophoric species j, and K_j is its specific absorption coefficient. Since elimination of chromophores in the delignification phase is accomplished by removal of lignin, we assume that the lignin content represents the chromophore content for a delignified pulp. Thus, we rewrite Eq. 38 as:

$$K = K_{\mathrm{LI}} \cdot C_{\mathrm{LI}} + c \qquad (39)$$

where the subscript LI denotes lignin, and c represents the contribution from the other components of pulp such as extractives and carbohydrates. However, the value of c is small compared to the product $K_{\mathrm{LI}} \cdot C_{\mathrm{LI}}$ because lignin is the main contributor to the light absorption in pulp. Thus, the Kappa number is directly proportional to lignin content, and a linear relationship exists between the initial light absorption coefficient of the D_1 stage and the Kappa number after the E_1 stage:

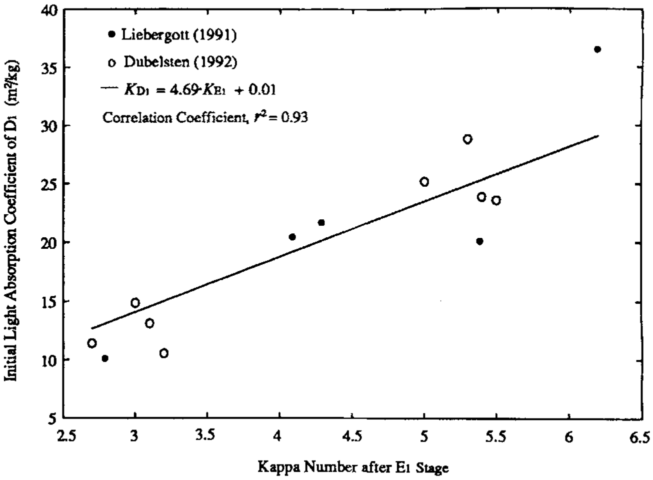

Figure 6. Light absorption coefficient vs. CE Kappa number.

$$K_{D_1,0} = b \cdot K_{E_1} + c \qquad (40)$$

As the nature of the chromophoric groups in pulp is not well characterized, values for b and c cannot be determined theoretically. We estimate b and c using data of Liebergott (1991) and Dubelsten (1992) that related the Kappa number following CE, C(E + O), (C + D)E and (C + D)(E + O) bleaching to the initial brightness entering the subsequent bleaching stages.

The Kubelka-Munk equation was used to convert brightness measurements to light absorption coefficient:

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2 \cdot R_\infty} \qquad (41)$$

where R_∞ denotes the reflectance of the pulp sheet to blue light at a 475 nm wavelength, that is, the brightness, and S is the light scattering coefficient. The value of the scattering coefficient varies from pulp to pulp. Here a value of 50 m²/kg was obtained from mill data and used to convert brightness values to light absorption coefficients and vice versa.

Fitting the published experimental data (Liebergott, 1991; Dubelsten, 1992) to Eq. 40 gives the following correlation between $K_{D_1,0}$ and K_{E_1}:

$$K_{D_1,0} = 4.69 \cdot K_{E_1} + 0.01 \qquad (42)$$

with a coefficient of correlation, $r^2 = 0.93$, as shown in Figure 6.

(C + D)EDED plant model

The input variables required for each stage of a bleach plant are shown in Figure 1. These include: the appropriate bleaching kinetic model and parameters; the stage temperature and liquor density; the mean residence time and flow parameters for the retention tower; the Norden efficiency and inlet and outlet consistency for the washer; the pulp flow rate, consistency, Kappa number or light absorption coefficient,

Table 3. Comparison between Simulated and Mill Data

Stage	Kappa No. or Brightness Simul.	 Mill	Residual Chem. (% on Liquor)	pH Simul.	 Mill.	Dissolved Solids (% on Liquor)
C+D	12.6		Cl_2: 3.25×10^{-2}	1.6		0.481
E	5.6	5.3	NaOH: 5.81×10^{-3}	11.2	11.0	0.628
D	74.9	75.3	ClO_2: 5.33×10^{-3} NaOH: 1.16×10^{-10}	3.5	3.7	0.169
E	74.9		NaOH: 9.60×10^{-2}	12.4		0.0893
D	88.8	89.2	ClO_2: 8.05×10^{-3} NaOH: 3.44×10^{-10}	3.9	3.8	0.0378

Unbleached pulp Kappa number = 25.2; operating conditions and experimental results from Dubelsten et al. (1992).

dissolved solids content, and pH entering the stage; and chemical content, pH, and flow rates of the chemical streams and recycled streams entering the stage. The model can simulate the dynamic responses of Kappa number after the delignification stages, the brightness after the brightening stages (D_1 and D_2), and the residual chemicals, pH, and dissolved solids in the process streams from each stage.

The accuracy of the model was judged by its ability to simulate the steady-state operation of an industrial-scale bleachery of softwood kraft pulp (Dubelsten et al., 1992). Detailed input data for the simulation is listed in Table 1 with the simulation results compared with the operating conditions in Table 3. Good agreement between the simulation and mill data are clearly seen.

Dynamic Behavior of a (C+D)EDED Plant

The dynamic (C+D)EDED plant model was used to investigate the effects of changes in (1) the chemical charge in the (C+D) stage, (2) the incoming Kappa number, and (3) the pulp production rate. We examined the Kappa number following the E_1 stage and the brightness after the D_1 and D_2 stages. The simulations were performed with no controllers in operation. Therefore, the results presented here are open-loop responses.

Although responses to step changes in chlorine charge, production rate and so on have been performed, we prefer to present the open-loop responses of the CE Kappa number and D_1 and D_2 brightness to variations in incoming Kappa number. The input Kappa number data were obtained from on-line measurements in a Swedish mill (Edlund, Lundquist and Hansson, 1992) and simulated by duplicating the magnitude and key frequencies of the measured disturbances. As shown in Figure 7a, large magnitude variations in the incoming Kappa number over a period of 5,000 min (3.5 days) proceeded quite slowly in comparison with the process dynamics. Consequently, they all passed through the system, resulting in the changes in CE Kappa number, CED and final brightness as shown in Figures 7b, 7c and 7d, respectively. The high frequency content of the disturbance is removed because of mixing.

We are now using this model to study the open- and closed-loop responses of an 850 t/d bleach plant in Western Canada.

Conclusions

A dynamic model for a (C+D)EDED bleach plant was presented using SIMNON as a simulation platform. A modular approach was followed with the key unit operations of mixing, retention, and washing modeled for each stage. Appropriate kinetics were incorporated using literature models modified as necessary. The delignification and brightening partial sequences of the bleach plant were linked using a correlation developed between the (C+D)E Kappa number and the chromophore content entering D_1 stage.

The model was used to study the dynamic behavior of the bleach plant to changes in production rate and chemical charge. The modular structure of the process allows a variety of bleach sequences to be assessed once pulp flow parameters and chemical kinetics are known.

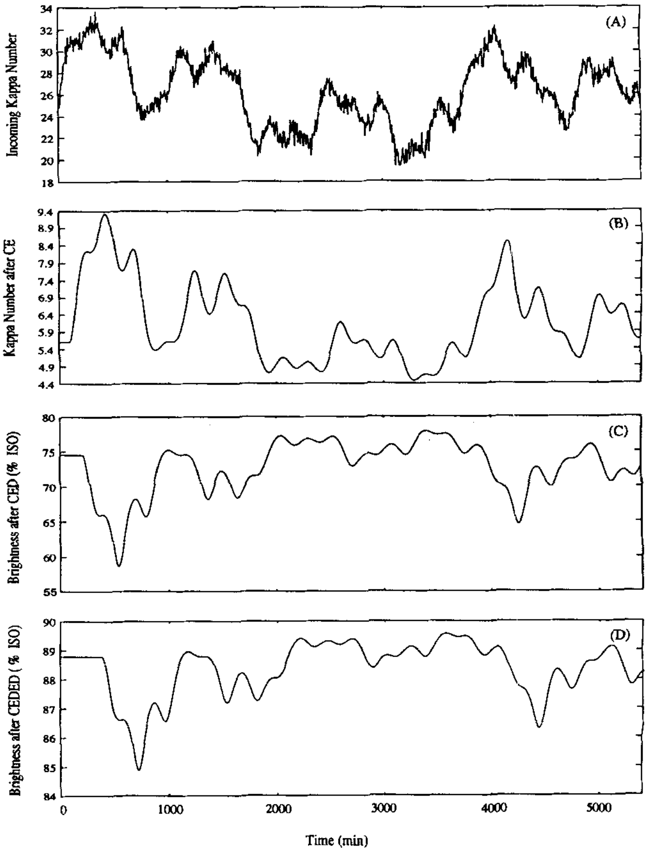

Figure 7. (C+D)EDED bleach plant dynamics to typical variations in incoming Kappa number.

(A) input, response in (B) CE Kappa number, (C) CED brightness and (D) CEDED brightness.

Notation

A_1 = constant in Eq. 33, $kg^2 \cdot m^{-4} \cdot min^{-1} \cdot mol^{-2} \cdot L^{0.2}$
A_2 = constant in Eq. 33, kg^2/m^4
A_3 = constant in Eq. 34, m^{2n}/kg^{n-1}
b = coefficient in Eq. 40, kg/m^2
B_1 = constant in Eq. 36, $kg^2 \cdot m^{-4} \cdot mol^{-0.1} \cdot L^{0.1} \cdot min^{-0.3}$
B_2 = constant in Eq. 37, $mol^{0.08} \cdot L^{-0.08} \cdot m^{-3} \cdot m^{2 \cdot n} \cdot kg^{1-n}$
c = constant in Eq. 40, m^2/kg
C_m = fiber consistency, % on slurry
E = residence time distribution, %/min
E_a = activation energy of bleaching reaction, kJ/mol
E_N = Norden efficiency factor, dimensionless
f = chlorine charge factor, % active Cl_2 on o.d. pulp/unbleached Kappa number
H_{st} = liquor level in seal tank, % on total tank level
K = content of chromophores, expressed as Kappa number in delignification stages (C and E_1), mL 0.1 N $KMnO_4$/g fiber, or light absorption coefficient in brightening stage (D_1, E_2 and D_2), m^2/kg
K_C = Kappa number in chlorination, mL 0.1 N $KMnO_4$/g fiber
K_{D_1} = light absorption coefficient in the first chlorine dioxide bleaching, m^2/kg
K_{E_1} = Kappa number in extraction, mL 0.1 N $KMnO_4$/g fiber
L = flow rate of liquor in pulp stream, kg/min
n = exponent
N_1, N_2 = number of CSTRs in series respectively before and after PFR
r = bleaching reaction rate, that is, rate of Kappa number decrease in a delignification, min^{-1} or rate of light absorption coefficient decrease in a brightening reaction, $kg^2 \cdot kg^{-1} \cdot min^{-1}$
R_∞ = reflectance at 457 nm (brightness), %ISO
RW = wash liquor ratio, dimensionless
S = light scattering coefficient, m^2/kg
t = time, min
$\bar{t}$ = mean residence time, min
$\bar{t}_c$ = mean residence time in CSTRs, min
$\bar{t}_p$ = residence time in PFR, min
$\bar{t}_t$ = mean residence time in retention tower, min
T = temperature, K
V = flow rate of liquor in nonpulp stream, kg/min
V_{st} = volume of seal tank, m^3
X = mass percentage of component in pulp liquor, %
Y = mass percentage of component in nonpulp liquor, %

Greek letters

ρ_l = liquor density, kg/m^3
Ψ = stoichiometric coefficient of bleaching reaction, % on o.d. pulp/(Kappa number) for delignification and % on o.d. pulp/(light absorption coefficient) for brightening

Subscripts

d = drum filter
f, s = fast and slow bleaching reactions
i = into process unit
j = bleaching liquor component, Cl_2, ClO_2, H^+, OH^- and DS (dissolved solids)
o = off process unit
r = recirculated
v = vat
0 = initial value of Kappa number or light absorption coefficient

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Manuscript received June 20, 1994, and revision received Nov. 22, 1994.

Correction

We would like to report two corrections to the parameters reported in Table 2 of the article titled "Effects of Kinetics on Residue Curve Maps for Reactive Distillation" (Vol. 40, p. 1814, 1994) by G. Venimadhavan, G. Buzad, M. F. Doherty, and M. F. Malone. The first is the Antoine coefficient C for MTBE. The number should read -48.406 instead of -34.42. The second is the binary interaction parameter for isobutene and MTBE. The coefficient A_{13} should read -60.1085 instead of -30.2477. In the first case, there was a mistake in transcribing the numbers from our source. In the second case, there was a typographical error in the source itself. Our results and conclusions are not significantly affected by these changes. At 8-atm pressure the boiling point of pure MTBE changes to 136.9°C, the composition of the methanol—MTBE azeotrope becomes 53.2% methanol and 46.8% MTBE with a boiling temperature of 120.29°C. The bifurcation in Figure 13 now occurs at $Da = 0.166$ instead of $Da = 0.143$. The sequence of maps in Figure 12 remains qualitatively unchanged, as do the conclusions in the article. We regret these errors and are sorry for any inconvenience thay may have caused.