Experimental pulping kinetics of Pinus radiata *cultivated in Chile*

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ABSTRACT: We adapted the Purdue model for kraft pulping kinetics for *Pinus radiata* wood cultivated in Chile. We cooked *P. radiata* chips in a batch kraft reactor at three different bulk temperatures (150°C, 160°C, and 170°C) and followed wood concentrations of lignin, cellulose, galactoglucomannans, and arabinoxylans along time for up to 3 h. We compared experimental data against the kinetic model and determined new optimal pre-exponential factors for each wood component at each temperature. The corrected kinetic model predicted experimental data fairly well for lignin, yield, cellulose, and galactoglucomannans but was less satisfactory for arabinoxylans. The modified pulping kinetics model is more suitable for describing kraft cooking of local *P. radiata* species and has been validated through successful simulation of an industrial Kamyr digester.

Application: *Pinus radiata* grown in Chile exhibits faster kinetics than those of northern softwoods. Pulp mills can use these findings to improve process control and optimize their industrial digesters.

Several fundamental kinetic models of the kraft pulping process are available in the literature. The Purdue model originally developed by Smith and Williams [1] characterized the composition of wood with five chemical and three liquor components. Diffusion effects in the wood chip were not considered. Christensen, et al. [2] modified the Purdue model using experimental data and a searching algorithm to optimize the kinetic parameters for different woods. They separated the woods into hardwoods and softwoods and found factors to correct the parameters for different kinds of species in each group. The corrections included factors applied to the frequency of the Arrhenius-type kinetic equations, the determination of a better high-to-low lignin ratio, the incorporation of residual concentration for some carbohydrates, and the incorporation of mass transfer parameters based on experimental data. Mass transfer was assumed to be limited by the diffusion between the surface of the wood and the bulk liquor, and the diffusion in the pores of the chips was ignored. Gustafson, et al. [3], developed a model to describe the combined effect of diffusion and kinetics within a wood chip. Agarwal and Gustafson [4] further improved the Purdue model by incorporating a three-dimensional diffusion in wood chips. Yang and Liu [5] proposed a new mechanism for the delignification reaction that takes into account the heterogeneous nature of the system and developed a kinetic model.

The widely used Purdue model has been validated with industrial data and offers a good compromise between phenomenological description and mathematical simplicity for computer solutions. Several authors had used the Purdue model in different engineering applications: Al-Awami and Sidrak [6] in process identification; Wisnewski and Doyle [7] and Al-Awami, et al. [8] in process control; and Wisnewski, et al. [9] in process simulation.

The Purdue model simulates a Kamyr continuous digester by approximating it as a three-phase plug flow reactor. The three phases are the wood, the liquor that has diffused into the wood or entrapped liquor, and the liquor that is available for free movement or free liquor. As these three phases interact the wood is digested into fiber and the hydroxide ions, hydrosulfide ions, and dissolved solids in the liquor change as the wood digests.

The five chemical components of wood composition of wood in the Purdue model are approximated by high-reactivity lignin, low-reactivity lignin, cellulose, galactoglucomannan (GM), and arabinoxylan (AX). The liquor is approximated by three components: hydroxide ions, hydrosulfide ions and dissolved solids for both the entrapped liquor and the free liquor, for a total of six liquor components. The diffusion of the three components between the two liquors is modeled through a mass transfer coefficient, and the consumption of entrapped liquor components is given by the rates of wood degradation reactions.

The wood and entrapped liquor are assumed to be at the same temperature. The free liquor transfers heat to and from the wood and entrapped liquor and involves two temperatures, the free liquor temperature and the wood-entrapped liquor temperature. Therefore, 13 variables describe the digester's dynamic behavior. In a batch digester, the entire system is considered to be at the same temperature.

The Purdue model was validated for several hardwoods

and softwoods cultivated in North America. We adapted the kinetics model to account for the chemical and physical difference of woods cultivated in Chile.

Füllgraff [10] tested the kinetic model modified by Christensen, et al. [2] against experimental batch kraft pulping data given by Godoy [11], Martínez [12], Jara [13], and Celulosa Arauco and Constitucion S.A., Arauco Plant, Chile [14]. Füllgraff [10] concluded that the Purdue kinetic model could be applied but specific kinetic parameters using experimental data compatible with the model's chemical characterization should be determined for *P. radiata* cultivated in Chile.

We carried out experimental kraft pulpings of *P. radiata* cultivated in Chile to obtain new and representative experimental data that would properly describe pulping kinetics using Arrhenius-type equations. The results would be applied in the simulation of an industrial pulp digester.

THE MATHEMATICAL MODEL

The Purdue model considers five wood components [lb/lb o.d. wood]: high-reactivity lignin (C_1), low-reactivity lignin (C_2), cellulose (C_3), galactoglucomannan (C_4), and arabinoxylan (C_5). In the kinetic model, hydroxide $(OH)_e$ and hydrosulfide $(SH)_e$ ions in entrapped liquor degrade the wood components and generate dissolved solids (X). The general form of reaction kinetics for all wood components is as follows [2]:

$$\frac{dC_j}{dt} = -\left[k_{S,j} \bullet [OH]_e + k_{K,j} \bullet [OH]_e^{0.5} \bullet [SH]_e^{0.5}\right] \bullet \left(C_j - C_{jU}\right) \quad (1)$$

The first term in Eq. 1 is called the soda reaction, in which OH^- ions hydrolyze lignin and carbohydrates and are consumed by reactions. The second term corresponds to the kraft reaction, in which SH^- ions are selective in the removal of lignin. C_{jU} corresponds to residual concentrations; and $k_{S,j}$ and $k_{K,j}$ are the frequency factors of reactions, whose dependence on temperature is given by Arrhenius-type relationships:

$$k_{S,j} = A_{S,j} \exp(-\Delta E_{S,j}/RT) \quad (2)$$

$$k_{K,j} = A_{K,j} \exp(-\Delta E_{K,j}/RT) \quad (3)$$

The entrapped liquor contents depend on their consumption by degradation of wood and on mass transfer between entrapped and free liquors. Mass balances for batch cooking can be written as follows:

$$\frac{d[OH]_e}{dt} = \frac{1}{V_e}\left[kA\left[[OH]_f - [OH]_e\right] + \left[b_{COH} - 0.5 \bullet b_{CSH}\right] \bullet \left(\frac{dL}{dt}\right) + b_{COH} \bullet \left(\frac{dC}{dt}\right)\right] \quad (4)$$

$$\frac{d[SH]_e}{dt} = \frac{1}{V_e} \bullet \left[kA \bullet \left[[SH]_f - [SH]_e\right] + 0.5 \bullet b_{CSH} \bullet \left(\frac{dL}{dt}\right)\right] \quad (5)$$

$$\frac{d[X]_e}{dt} = \frac{1}{V_e} \bullet \left[kA \bullet \left([X]_f - [X]_e\right) - \left(\frac{dW}{dt}\right)\right] \quad (6)$$

where $L = C_1 + C_2$ is total lignin content, $C = C_3 + C_4 + C_5$ is total carbohydrate content, and $W = L + C$ is total wood content; kA is the mass transfer coefficient; b_{COH}, b_{CSH}, and b_{COHC} are stoichiometric coefficients for consumptions of OH^- by lignin, SH^- by lignin, and OH^- by carbohydrates, respectively [2]. Finally, V_e is the volume of entrapped liquor within the chips. Corresponding mass balances for free liquor components are:

$$\frac{d[OH]_f}{dt} = -\frac{1}{V_f} \bullet kA \bullet \left[[OH]_f - [OH]_e\right] \quad (7)$$

$$\frac{d[SH]_f}{dt} = -\frac{1}{V_f} \bullet kA \left[[SH]_f - [SH]_e\right] \quad (8)$$

$$\frac{d[X]_f}{dt} = -\frac{1}{V_f} \bullet kA \bullet \left[[X]_f - [X]_e\right] \quad (9)$$

where V_f is the volume of free liquor that surrounds the chips. Model Eqs. 1–9 are solved numerically and the results are compared with experimental data. Initial concentrations of lignin C_1 and C_2 are calculated from the initial concentration and from the initial ratio of high-to-low reactivity lignin (between 10/90 and 30/70) [2]. Initial concentrations of the entrapped liquor components are zero, and initial concentrations of free liquor components are calculated from the liquor-to-wood ratio, the sulfidity of liquor, and the extractives concentration in wood. The solution of Eqs. 7 and 8 predicts residual effective alkali concentration.

EXPERIMENTAL

A pile of about 900 kg of *P. radiata* chips was mixed and divided into quarters. One quarter was sifted, and chips that were larger than 45 mm, thicker than 10 mm, and smaller than 7 mm (fines) were discarded. The sieved chips provided 12 samples that were selected for moisture analysis (TAPPI T 258 om-94 "Basic density and moisture content of pulpwood") and had an average moisture content of 57.4% (wet basis). The remaining material was divided into 30 samples of 2.8 kg each (o.d. wood) for pulping experiments. Experimental runs were carried out in a laboratory-scale batch digester, heated by continuous recirculation of liquor with external heating. A temperature control loop adjusted the steam flow to the external heat exchanger to maintain the desired temperature trajectory.

The initial cooking temperature was 87ºC for all samples, and the ramp time to reach bulk cooking temperature was 2 h. The bulk experimental temperatures were 170°C, 160°C, and 150ºC. To monitor the extent of reactions, five cooking experiments were run in duplicate at each temperature and the batches stopped at five time intervals. For 160C° and 170ºC the cooking times were 1.0, 1.5, 2.0, 2.5, and 3.0 h; for 150ºC corresponding times were 1.5, 2.0, 2.5, 3.0, and 3.5 h. At the end of each batch the temperature was dropped by cold water

washing after lowering the pressure in the digester. Liquor-to-wood ratio was 4 (L/kg), initial effective alkali concentration was 18%, and initial sulfidity was 29.7%. Samples of wood and liquor were prepared for analysis according to TAPPI T 257 cm-85 "Sampling and preparing wood for analysis" and T 264 cm-97 "Preparation of wood for chemical analysis." All the experimental work was performed at the laboratory facilities of an industrial plant (Celulosa Arauco, Chile). Lignin content was analyzed according to TAPPI T 222 om-98 "Acid-insoluble lignin in wood and pulp" or T 236 cm-85 "Kappa number of pulp" and residual alkali according to TAPPI T 625 cm-85 "Analysis of soda and sulfate black liquor." Yield was calculated as the mass ratio (dry basis) of wood after each batch to the initial wood feed.

In the first and second batch samplings, the chips appeared to be uncooked although some of the material had been dissolved; the third sampling showed partially cooked chips, and pulp was obtained in the last two samplings. Carbohydrate contents in wood (including raw chips) were sent for analysis to the Laboratory of Cellulose and Paper, Federal University of Vicosa, Brazil. The report by Colodette and Gomes [15] described the analytical techniques, which were grinding and screening (40/60 mesh) of wood or pulp; sulfuric acid hydrolysis according to TAPPI T 249 cm-85 "Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography"; and filtration of hydrolyzed liquor and carbohydrate analysis by high performance liquid chromatography (HPLC) (Shimadzu Class-VP V 5.02, Aminex column HPX-87 P).

The percent content of galactose, mannose, xylose, arabinose, and glucose was reported [15]. The initial composition of raw pine was: cellulose 52.77%, GM 14.09%, AX 6.17%, lignin 23.97%, and 3% extractives and ashes. Cellulose concentrations were calculated from glucose and mannose contents [16].

THE OPTIMIZATION ALGORITHM

We used a searching algorithm written in Matlab and communicated with the Fortran simulation program to find the specific kinetic parameters for the pulping simulation of *P. radiata* cultivated in Chile. The frequency factors $k_{S,j}$ and $k_{K,j}$ of Eq. 2 and 3 from the Purdue model are multiplied by corresponding correction factors to be found from experimental pulping data for *P. radiata*. These factors modify only the pre-exponential factors of Eq. 2 and 3, since the activation energies remained unchanged. The 10 correction factors for five wood components have been combined into four: one factor for the four lignin kinetic parameters, one for the two cellulose parameters, one for the two GM parameters, and one for the two AX parameters. In the Purdue model, these factors work as tuning parameters for the particular kinetics of *radiata* pine. The searching algorithm minimizes the sum of squares of the difference between experimental and simulated data for the wood components lignin, cellulose, GM, and AX using Eq. 10. For each iteration the Matlab program calculates a correction factor $F_{i+1,j}$ using Eq. 11.

$$S_i = \sum_{j=1}^{4}\left(\sum_{k=1}^{n}\left(P_{i,j,k} - M_{j,k}\right)^2\right) \quad \text{(lb/lb o.d. wood)} \quad (10)$$

$$F_{i+1,j} = \prod_{0}^{i} F_{i,j} \bullet (1 + C_{i,j} \bullet S_i) \quad (11)$$

where:

- S_i = sum of the squares of the difference between experimental and simulated data;
- $P_{i,j,k}$ = simulated value in the *i* iteration for the *j* component at the *k* time;
- $M_{j,k}$ = experimental value for the *j* component at the *k* time;
- $F_{i+1,j}$ = new correction factor;
- $F_{i,j}$ = correction factor ($F_{0,j}$=1);
- $C_{i,j}$ = constant (the sign depends on the S_i behavior [increases or diminishes] and the value depends on the wood component optimized kinetic parameter; the values were empirically determined);
- i = iteration number;
- j = wood component (lignin, cellulose, galactoglucomannans, or arabinoxylans);
- k = data time; and
- n = number of experimental values for each component.

New correction factors were calculated by adjusting previous values, and the program iterates until a convergence criteria is satisfied: the $S_{i+1} - S_i$ difference must reach a specified minimum value. Eqs. 10 and 11 are applied in a sequence. First they are solved to find out the optimal correction factor for lignin components, while all other correction factors are set equal to one. Once the objective function is so minimized, Eq. 10 is restated in terms of the corrected factor for lignin. The optimization algorithm is next applied to solve for the optimal correction frequency factor for cellulose, keeping as one the factors for the last two components. The procedure is repeated until all corrected factors are determined. This order of priority was selected because kappa number and cellulose are the most important responses of kraft pulping. During the search the objective function is reduced from a starting value (original Purdue model) to its minimum value (optimal parameters).

RESULTS AND DISCUSSION

The optimization algorithm generated new Arrhenius kinetic parameters and we obtained a new kinetic model for the experimental data. In this section, we discuss the correction factors, the objective function, and the improvements in the simulations.

Table I shows original parameters, correction factors of pulping kinetics for *P. radiata*, the objective function, and

	Purdue model	Correction factor			Objective function			Normalized objective function		
	$ft^3/lb{\cdot}h$	170°C	160°C	150°C	170°C	160°C	150°C	170°C	160°C	150°C
					0.005125*	***0.005012****	***0.005304****	1.00	1.00	1.00
High-reactivity lignin-Soda	2,70E+02	1.53	1.25	0.98	0.003839	0.004649	0.005291	0.75	0.93	1.00
High-reactivity lignin-Kraft	8,90E+03	1.53	1.25	0.98	0.003839	0.004649	0.005291	0.75	0.93	1.00
Low-reactivity lignin-Soda	5,80E+13	1.53	1.25	0.98	0.003839	0.004649	0.005291	0.75	0.93	1.00
Low-reactivity lignin-Kraft	4,74E+02	1.53	1.25	0.98	0.003839	0.004649	0.005291	0.75	0.93	1.00
Cellulose-Soda	6,20E+03	1.53	1.27	0.96	0.002721	0.003870	0.005156	0.53	0.77	0.97
Cellulose-Kraft	2,70E+04	1.53	1.27	0.96	0.002721	0.003870	0.005156	0.53	0.77	0.97
Galactoglucomannan-Soda	1,50E+03	2.32	1.64	1.29	0.001605	0.003245	0.004978	0.31	0.65	0.94
Galactoglucomannan-Kraft	1,00E+04	2.32	1.64	1.29	0.001605	0.003245	0.004978	0.31	0.65	0.94
Arabinoxylan-Soda	9,80E+06	1.53	1.27	1.00	0.001459	0.003058	0.004978	0.28	0.61	0.94
Arabinoxylan-Kraft	5,50E+19	1.53	1.27	1.00	0.001459	0.003058	0.004978	0.28	0.61	0.94

I. Pre-exponential factors of the original kinetic model ($ft^3/lb{\cdot}h$), correction factors, objective functions, and normalized objective functions for 170°C, 160°C, and 150°C. * Starting value for the original Purdue model.

	% Average errors (170°C)			% Average errors (160°C)			% Average Errors (150°C)		
	Corrected model	Original model	Experimental	Corrected model	Original model	Experimental	Corrected model	Original model	Experimental
Lignin	9.8	39.6	2.5	6.8	11.6	0.7	2.3	2.5	3.9
Cellulose	2.1	3.5	0.3	3.1	4.0	0.5	4.3	4.5	0.4
Galactoglucomannan	8.4	27.4	1.4	6.2	16.5	1.0	7.5	9.4	2.9
Arabinoxylan	19.2	20.5	2.1	33.7	36.3	1.5	37.3	37.3	1.2
Yield	1.5	9.0	0.3	4.2	8.2	0.9	3.4	3.7	2.3
Residual effective alkali	17.7		12.1	3.7		7	5.7		6.1

II. Modeled errors of original and corrected kinetics and experimental errors.

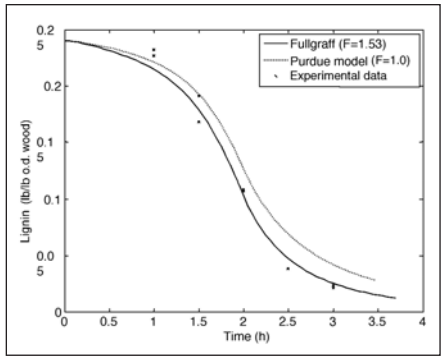
the normalized objective function. **Table II** shows average errors for the corrected model, for the original model, and for the experimental data. All cooking runs were carried out in duplicate, and experimental errors were calculated from data analysis.

At a bulk temperature of 170°C, **Figs. 1–5** show the simulations using the original kinetic parameters, the simulation using the correction factors for the kinetic of each wood component, and the experimental data. Figs. 1–5 correspond to lignin, yield, cellulose, GM, and AX, respectively. **Table III** presents the experimental data.

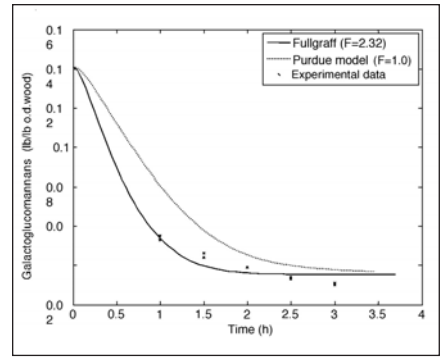
The correction factor for the four frequency factors of lignin kinetics is 1.53, the objective function drops to 75% of its starting value, and the average modeled error diminishes from 39.6% to 9.8%. The correction factor for the two frequency factors of cellulose kinetics is 1.53, the objective function reduces to 53% of the initial value, and the average error diminishes from 3.5% to 2.1%. The correction factor for the two frequency factors of GM kinetics is 2.32, the objective function reduces to 31% of the initial value, and the average error lessens from 27.4% to 8.4%. The correction factor for the two fre-

Time	Lignin	Yield	GM	AX	Cellulose	Residual effective alkali
Minutes	*lb/lb o.d wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/ft^3*
0	0.25 0.23	0.97 0.97	0.14 0.15	0.06 0.06	0.53 0.52	2.3 2.34
60	0.23 0.23	0.81 0.81	0.05 0.05	0.05 0.05	0.47 0.47	1.46 1.31
90	0.17 0.19	0.73 0.74	0.04 0.05	0.05 0.05	0.46 0.45	1.17 1.09
120	0.11 0.11	0.61 0.61	0.04 0.04	0.04 0.04	0.44 0.44	0.69 1.00
150	0.04 0.04	0.52 0.52	0.03 0.03	0.04 0.03	0.42 0.42	0.56
180	0.02 0.02	0.49 0.49	0.03 0.03	0.03 0.03	0.42 0.42	0.24 0.36

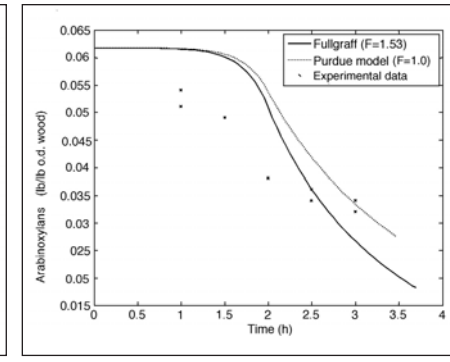
III. Experimental data of kraft pulping for* P. radiata *at 170°C.



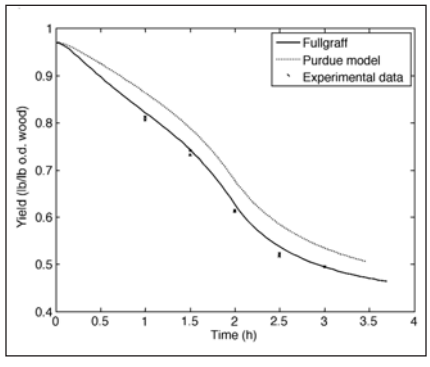
1. Lignin (lb/lb o.d. weight) as function of time (h) for 170ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and experimental data (crosses).



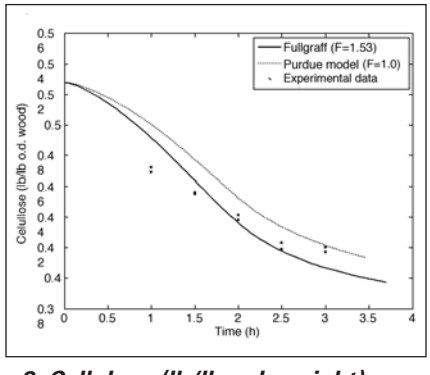
4. Galactoglucomannans (lb/lb o.d. weight) as function of time (h) for 170ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and HPLC experimental data (crosses).



5. Arabinoxylans (lb/lb o.d. weight) as function of time (h) for 170ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and HPLC experimental data (crosses).



2. Yield (lb/lb o.d. weight) as function of time (h) for 170ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and experimental data (crosses).



3: Cellulose (lb/lb o.d. weight) as function of time (h) for 170ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and HPLC experimental data (crosses).

quency factors of AX kinetics is 1.53, the objective function drops to 28% of the initial value, and the average error decreases from 20.5% to 19.2%. Modeled errors are mostly attributed to the simplicity of characterization of wood and liquors and to the postulated kinetics in a complex process.

Table II shows that experimental errors are less than modeled errors, particularly at high temperatures. The average error for yield simulations reduces from 9.0% to 1.5%. The worst results were obtained for AX simulation, where no better factor can be determined without affecting negatively the other results, due to the high degree of interaction among the kinetic relationships of wood components. Tables I and II also show results for pulpings of *P. radiata* at bulk temperatures of 160ºC and 150ºC, and **Tables IV** and **V** present the experimental data. Correction factors increase at higher temperature and are greater than one at 170ºC and 160ºC, and almost one for 150ºC. This means that *P. radiata* cultivated in Chile reacts faster than northern softwood, as

Time	Lignin	Yield	GM	AX	Cellulose	Residual effective alkali
Minutes	*lb/lb o.d wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/ft³*
0	0.25	0.97	0.14	0.06	0.53	2.3
	0.23	0.97	0.15	0.06	0.52	2.34
60	0.23	0.80	0.06	0.05	0.46	1.34
	0.23	0.82	0,06	0.05	0.47	1.59
90	0.20	0.76	0.05	0.05	0.45	1.17
	0.20	0.76	0.05	0.05	0.46	1.34
120	0.15	0.67	0.04	0.04	0.45	1.06
	0.14	0.68	0.04	0.05	0.44	0.91
150		0.59	0.04	0.04	0.45	0.96
	0.10	0.61	0.04	0.04	0.44	0.84
180	0.06	0.53	0.04	0.04	0.41	0.71
	0.06	0.55	0.04	0.04	0.42	0.80

IV. Experimental data of kraft pulping for* P. radiata *at 160ºC.

Time	Lignin	Yield	GM	AX	Cellulose	Residual effective alkali
Minutes	*lb/lb o.d wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/lb o.d. wood*	*lb/ft³*
0	0.25	0.97	0.14	0.06	0.53	2.3
	0.23	0.97	0.15	0.06	0.52	2.34
90	0.20	0.75	0.05	0.05	0.45	1.17
	0.23	0.77	0.05	0.05	0.45	1.39
120	0.18	0.73	0.04	0.05	0.46	1.22
	0.18	0.72	0.05	0.05	0.46	1.06
150	0.16	0.75	0.04	0.05	0.50	1.02
	0.14	0.68	0.04	0.05	0.49	1.12
180	0.12	0.52	0.04	0.05	0.45	0.83
	0.12	0.64	0.04	0.05	0.45	0.86
210	0.11	0.66	0.04	0.04	0.42	0.87
	0.10	0.60	0.04	0.04	0.43	0.73

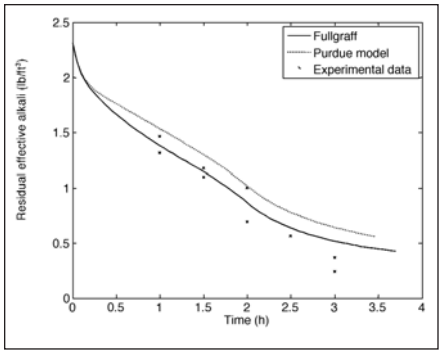
V. Experimental data of kraft pulping for* P. radiata *at 150ºC.

reported by Christensen et. al. [2], and the behavior increases as temperature becomes higher. Because chemical reactions depend on temperature, reactivity differences between both pine species are expected to become more pronounced at 170ºC, where correction factors for *P. radiata* are greater. Reactivity differences between *P. radiata* and northern softwood at 170ºC are also expressed by strong descents of the objective function after each optimization sequence (see Table I). At lower temperatures the reactivity deviations of *P. radiata* from northern softwood are much smaller, correction factors approach to unity, and the objective function changes little. We emphasize that the Purdue model was developed to simulate conventional pulping at bulk temperatures near to 170ºC, the condition at which major discrepancies can be expected for different pine species.

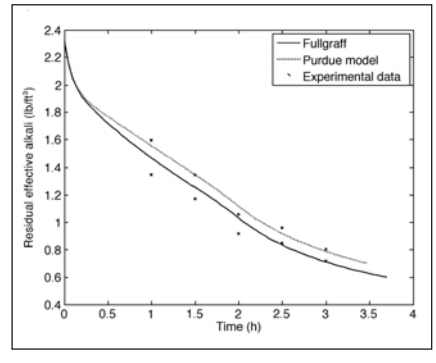
The final effective alkali concentrations in the free liquor were simulated with the original and with the corrected kinetic parameters. **Figures 6–8** show the simulations at 170ºC, 160ºC, and 150ºC, and experimental data at all three temperatures are presented in Tables III–V. Average modeled and experimental errors are given in Table II. At 170ºC and 160ºC, the original kinetics predict alkali concentration by excess when compared with experimental data and alkali consumption proceeds more rapidly than Purdue model prediction. The departure between modified and original kinetic curves in Figs. 6 and 7 reinforces the conclusion on reactivity differences of *P. radiata* with northern softwood. At 150ºC, no significant differences can be seen (see Fig. 8).

Mass transfer of OH, SH, and X, between entrapped and free liquors is not important in batch cooking because concentration differences are too small and wood degradation is controlled by chemical reactions. In a continuous reactor with an impregnation zone, with liquor injections and extractions and with a washing zone, mass transfer is important because concentration differences between both liquors are much higher. Mass transfer experiments in wood chips cannot be carried out in the absence of chemical reactions because chemical reactions consume the liquor components and mass transfer coefficients are difficult to determine.

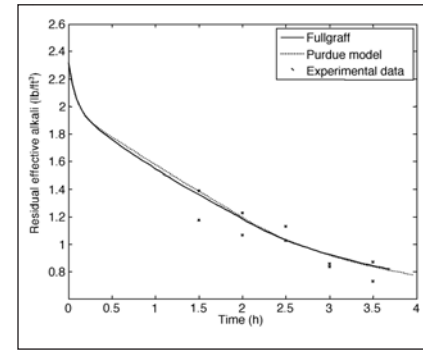
The modified kinetics for *P. radiata* was later applied by Araneda [17] to sim-



6. Residual effective alkali concentrations in the free liquor (lb/ft³) as function of time for 170ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and experimental data (crosses).



7. Residual effective alkali concentrations in the free liquor (lb/ft³) as function of time for 160ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and experimental data (crosses).



8. Residual effective alkali concentrations in the free liquor (lb/ft³) as function of time for 150ºC bulk temperature. Original kinetic model (dotted line), corrected kinetic model (solid line), and experimental data (crosses).

ulate the operation of a two- vessel continuous industrial LoSolid pulp digester (Celulosa Arauco, Chile), using the Purdue model. Araneda also corrected the compaction factor of chips from manufacturers' design data. The Purdue model was adapted to the digester's geometry, configuration of streams, and operational conditions. Simulated results predict well the blow-line kappa number (about 30), yield (about 46%), free liquor temperature profile, and pulp throughput (about 1250 a.d. tons/day), for four steady-state cases of the Kamyr digester. The simulation also predicts alkali, sulfidity, and dissolved solids profiles, but there are no industrial data for comparison.

CONCLUSIONS

From experimental data, we obtained a corrected kinetic model of kraft pulping of *P. radiata* grown in Chile. The model follows Christensen et al. kinetics [2], and pre-exponential factors for pulping reactions were improved through correction factors for each component of wood. We concluded that P. radiata reacts faster than northern softwood for which Christensen kinetics was constructed. The modified kinetics corresponded well with experimental data of batch kraft pulpings for lignin content and yield. Modeled simulations for GM, cellulose, and residual effective alkali concentrations are acceptable, while model predictions for AX are poor. The corrected kinetic model for P. radiata was validated in the successful simulation of an industrial Kamyr digester. **TJ**

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INSIGHTS FROM THE AUTHORS

We did this study on pulping kinetics of Pinus *radiata* cultivated in Chile because of the economic importance of the pulp and paper industry to Chile. Our work follows the structure of the Purdue model, but makes modifications for Chilean-grown P. *radiata*.

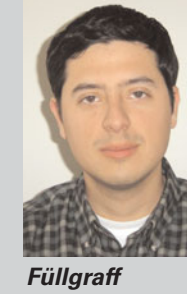
The most challenging aspect of this research was to characterize the components of the wood; this work was performed in a specialized laboratory in Brazil.

The most interesting finding was that P. radiata grown in Chile exhibits faster kinetics than that of the northern softwood reported in the Purdue model. Pulp mills can use these findings to improve process control and optimize their industrial digesters.

Our next step is to apply the results in a mathematical simulation of a local industrial pulp digester and compare those findings with actual pulping data.

Melo

Canales



Füllgraff

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