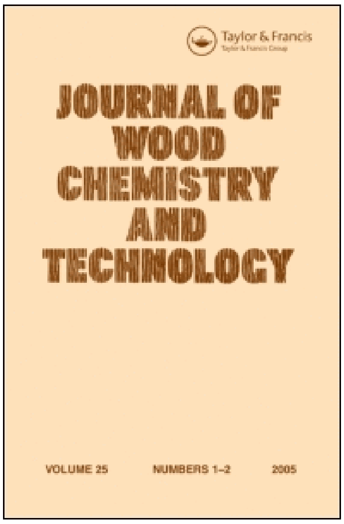

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DEVELOPMENT OF MATHEMATICAL MODELS FOR DESCRIBING ORGANOSOLV PULPING KINETICS OF FUNGALLY PRETREATED WOOD SAMPLES

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ABSTRACT

Eucalyptus grandis wood samples decayed by white- and brown-rot fungi were cooked at 180°C for 5 to 100 min with methanol/water (78:22 v/v) containing 25 mM of $CaCl_2$ and 25 mM $MgSO_4$. Mathematical models for describing organosolv pulping kinetics of the fungally pretreated samples were developed to estimate delignification constants, and also rate constants for xylan and wood mass solubilization. These models had high R^2 values and were able to predict pulp yield, as well as lignin and xylan contents during the process at 99% confidence level. Delignification of undecayed control samples had a rate constant of 2.0 $\times 10^{-2}$ min^{-1} for the bulk phase. Most decayed samples presented delignification constants higher than those of the control. Some decayed samples exhibited an additional delignification phase at the beginning of the process, which was characterized by a low solubilization rate. These samples required insertion of an additional term in the model to represent this phase.

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INTRODUCTION

Organosolv pulping has been claimed as an environmentally friendly technique for obtaining cellulose pulps. This process can avoid problems caused by sulfur emissions. Moreover, integral use of wood components and low capital investment costs are advantages that make small-scale pulp mills feasible.[1-4]

Pulp production by organosolv processes has been evaluated using several wood species and a broad range of organic solvents in acidic or alkaline media. Despite the high delignification efficiency of several acid-catalyzed organic solvent systems, acidic conditions can result in carbohydrate degradation. Carbohydrate degradation occurs in acid-catalyzed organosolv pulping because of high temperature or high acid concentration necessary to provide efficient delignification. As a consequence, pulps with low papermaking quality are obtained.[5-6]

It has been postulated that if the lignin macromolecule is partially depolymerized in an initial step, mild cooking conditions are feasible and carbohydrate degradation can be prevented. This pretreatment can be carried out by fungal degradation of wood chips using selective white-rot fungi.[7-9] Fungal pretreatment provides faster delignification rates in acid-organosolv pulping processes. As a consequence, the same residual lignin contents in the fungal-pretreated samples are achieved at shorter reaction times, which means energy saving and pulps of increased strength properties.

The effects of fungal pretreatment on chemical pulping processes are usually greater if the cooking is carried out at low severity.[7-10] Therefore, fungal pretreatment followed by pulping using low temperature or short cooking time should present the best results combining wood biodegradation and chemical pulping. In this regard, a kinetic study of pulping would help to evaluate the actual effects of the fungal pretreatment.

Evaluating delignification rates in a heterogeneous group of samples (undecayed, white- and brown-rotted for varied biodegradation times) is a difficult task, because delignification kinetics differ from one sample to another, since these samples are chemically and ultrastructurally modified.[9,11-12] This paper focuses on the development of mathematical models for estimating delignification rate constants and also rate constants for xylan and wood mass solubilization in organosolv pulping of fungally pretreated samples. A group of samples, decayed for varied periods of time by white- and brown-rot fungi,[8] was used to cover all types of wood biodegradation and to provide representative results.

EXPERIMENTAL

Wood Preparation

Freshly cut chips (approximately 2.5 x 1.5 x 0.2 cm) of 8-year-old trees of *E. grandis* were kindly furnished by a local fiberboard mill. Wet chips were air-dried to a final humidity of 8-10% and stored in dry conditions until utilization. Before incubation, 50 g of wood chips were immersed in water for 12 h. Afterwards, the water was drained and the humid chips were sterilized at 121°C for 15 min. Sterilized wood chips were cooled and used in the biodegradation experiments[7]. This procedure was also used to prepare the undecayed control samples.

Fungi, Inoculum Preparation and Wood Biodegradation

The white-rot fungus used in this work was *Punctularia artropurpurascens*, kindly furnished by Dr. L. Bettucci from Facultad de Ciencias, Universidad de la Republica de Montevideo, UY. The brown-rot fungus was *Wolfiporia cocos* ATCC 62778.

The fungi were grown on 200 mL of 2% malt-extract-solid-medium in 2 L Erlenmeyer flasks for 7-10 days. After fungal growth on the medium surface, 50 g of sterilized wood chips was added to the cultures and hand-shaken for homogenization.[7] Cultures were maintained stationary at 27°C for periods between 15 days and 4 months. Growth was stopped after defined periods by washing all mycelium from the surface of the chips. Decayed chips were dried to constant weight at 100°C. Weight loss was determined on the basis of the initial and final dry weights. The undecayed control samples were also dried at 100°C to constant weight and the weight loss due to the autoclaving procedure (1.5 %) was subtracted from weight loss data of decayed samples.

Organosolv Delignification

Wood chips were delignified by an organosolv system using a wood/liquor ratio of 1:10. The solvent system was methanol/water (78/22 v/v) with $CaCl_2$ and $MgSO_4$ salts (25 mM of each).[13] The cooking process was performed at 180°C for reaction times varying from 5 to 100 min. Stainless-steel reactors (80 mL and 200 mL) were used. Small reactors (80 mL) were heated in a silicone oil bath at a final temperature of 180°C. Larger reactors (200 mL) were heated by an electrical heating device and the internal temperature was measured with a thermocouple. In both cases, after heating for a defined reaction time, the reactor was cooled in water. The residual unclassified pulp was vacuum filtered and then washed once with 1 L of water and three times with 200 mL of acetone/water (9/1 v/v).[7]

H-factor[14] values were used to correct the heating-up time necessary to reach 180°C and any occasional fluctuation of the maximum temperature. Reported data were expressed in equivalent time at maximal cooking temperature (180°C). The H-factor was estimated based on plots of relative reaction rate constant as a function of cooking time. The area under these plots for each reaction furnished the reaction H- factor. Relative reaction rate constants were calculated on the basis of Arrenhius equation using an average activation energy of 80 kJ/mol for the organosolv delignification.[4] The relative reaction rate constant was assumed as the unit for the temperature of 100°C.[14]

Chemical Analysis of Wood and Pulp Samples

Wood and pulp samples were milled in a knife mill to pass through a 0.5 mm screen. Milled wood was extracted with 95% ethanol for 6 h in a soxhlet apparatus to remove extractives. Extractive contents determination was based on dry weight of raw and extracted wood samples. Pulps produced at several reaction times were not previously extracted. Extracted wood or pulp samples were hydrolyzed with 72% sulfuric acid at 30°C for one hour (300 mg of sample and 3 mL of sulfuric acid). The acid was diluted to a final concentration of 3% by addition of 79 mL of water and the mixture was heated in an autoclave at 125°C for one hour. The residual material was cooled and filtered through porous glass filter number 3. The solids were dried at 105°C to constant weight and determined as insoluble lignin. The concentrations of monomeric sugars in the soluble fraction were determined by HPLC using a BIORAD HPX87H column operated with 0.005 mol.L^{-1} sulfuric acid at 0.6 mL.min^{-1}. Sugars were detected by a 25°C-thermostatized RI detector. Polymeric glucan and xylan were calculated as monomeric glucose and xylose contents multiplied by 0.9 and 0.88, respectively[7]. The soluble lignin concentration in the filtrate was determined by measuring the absorbance at 205 nm and using the value of 105 $\text{L.g.}^{-1}\text{cm}^{-1}$ as absorptivity of the soluble lignin.[15] All analyses were performed in duplicate.

RESULTS AND DISCUSSION

Development of a Mathematical Model for Describing Organosolv Pulping Kinetics of Undecayed *Eucalyptus grandis* Wood Chips

Figure 1 shows the experimental data for the solubilization of *E. grandis* wood components during organosolv pulping by the methanol/water-earth alkali metal salts system. Residual lignin drops rapidly in the first 40 minutes of cooking (Figure 1). This lignin removal was followed by fiber separation, as evidenced by

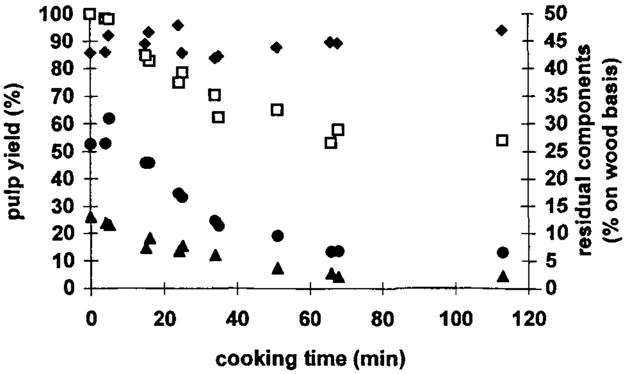

Figure 1. Solubilization of wood and wood components of undecayed *Eucalyptus grandis* during organosolv delignification by methanol/water (78:22 v/v) containing 25 mM of $CaCl_2$ and 25 mM $MgSO_4$ at 180°C.(□) pulp yield; (●) lignin; (▲) xylan; (◆) glucan.

easy hand disruption of cooked chips along the fiber axis. This pulping method was previously described as being efficient for delignification of black spruce softwood (*Picea mariana*).[13] In this case, middle lamella lignin removal at the initial delignification stages was evidenced by STEM-EDXA studies of brominated samples.

Plots showing the pulp yield as a function of the residual lignin and xylan contents, that represents pulping selectivity, are presented in Figure 2. These plots showed a linear relationship up to 6% residual lignin contents (wood basis). Lower values of residual lignin were not achieved at this pulping temperature.

The development of mathematical models for describing pulping kinetics was initially based on the experimental data presented in Figures 1 and 2. Figure 1 shows two consecutive and distinct phases for the pulp yield as a function of the cooking time. The first phase is characterized by a fast solubilization of wood chips following a nonlinear decay of the pulp yield as cooking time increases (bulk phase). In the second phase, the solubilization rate decreases significantly and pulp yield approximates to a limit value (residual phase). Assuming an

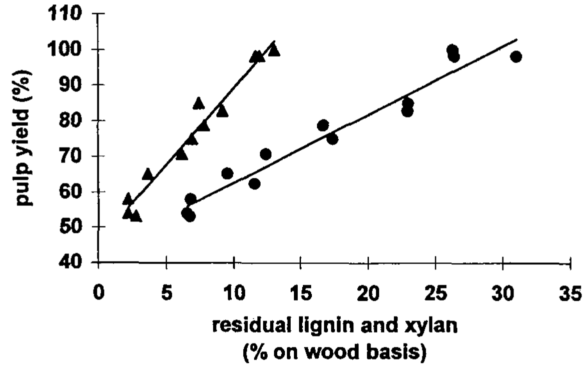

Figure 2. Pulp yield as a function of the residual lignin and xylan contents in unclassified organosolv pulps of *Eucalyptus grandis* delignified by methanol/water (78:22 v/v) containing 25 mM of $CaCl_2$ and 25 mM $MgSO_4$ at 180°C. (●) lignin; (▲) xylan.

exponential type decay for the bulk phase, and considering that the residual phase can be modeled by term **($1-Y^*/Y$)**, equation **1** can describe the pulp yield at all pulping stages.

$$\frac{dY}{dt} = -k_Y Y\left(1 - \frac{Y^*}{Y}\right) \quad (1)$$

In this equation **Y** is the pulp yield, **Y^*** is the limit value of pulp yield, **t** is the cooking time, and **k_Y** is the rate constant for wood solubilization. The solution of the equation **1**, satisfying the initial condition **$Y = Y_0$** for **$t = 0$** is shown in equation **2**.

$$Y = (Y_0 - Y^*)e^{-k_Y t} + Y^* \quad (2)$$

Parameters **Y^*** and **k_Y** can be determined by fitting this model to the experimental data. This was carried out by nonlinear regression using the Marquardt's numerical method.[16]

This model (equation **2**) was consistent with the experimental data obtained for the delignification of *E. grandis* wood (Figure 1). For short cooking times the exponential term predominates, while at the end of cooking, this term approximates to zero, and **Y** approximates to $\mathbf{Y}^*$.

The kinetics of delignification and xylan removal, where two or even three solubilization phases can be defined, is usually modeled by similar equations.[4,17-18] Although these models work well for undecayed samples, they are not suitable for large groups of fungally pretreated samples where the kinetic behavior is not known. Actually, the replacement of yield values by residual lignin or xylan contents in equation **2**, to estimate rate constants for lignin and xylan removal, resulted in the estimation of statistically insignificant parameters for several samples (data not shown). Some samples presented fast bulk delignification phases and only 2 or 3 points were available for estimating rate constants. Moreover, several biodegraded samples presented an additional and slow delignification phase at the beginning of the process.

On the other hand, for all cases (decayed and undecayed samples), the residual lignin or xylan contents in organosolv pulps are linearly correlated with pulp yield, independently of the pulping phase, as illustrated in Figure 2 for the undecayed control. Based on these linear relationships, as well as on equation **2**, residual lignin and xylan contents were simulated at several cooking times. This simulation allowed the building of plots with a larger number of points as shown in Figure 3. These simulated points were used for an estimation of the rate constant values for delignification and xylan removal based on pseudo-first-order kinetic plots, as shown in Figure 4. Rate constant value for the bulk delignification phase of the undecayed control was 2.0×10^{-2} min^{-1}, which was close to delignification rates reported both for *Picea mariana* softwood (1.8×10^{-2} min^{-1}) treated by the same organosolv process carried out at 200°C[13] and for *Eucalyptus globulus* hardwood (2.9×10^{-2} min^{-1}) cooked with 50% ethanol at 185°C[19]. The same model made it possible to predict the time necessary for the phase to change

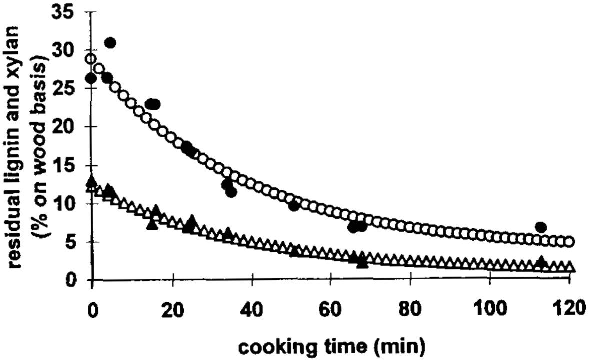

Figure 3. Experimental (black filled) and simulated values (open symbols) of residual lignin and xylan contents in unclassified organosolv pulps of *Eucalyptus grandis* delignified by methanol/water (78:22 v/v) containing 25 mM of $CaCl_2$ and 25 mM $MgSO_4$ at 180°C. (●) lignin; (▲) xylan.

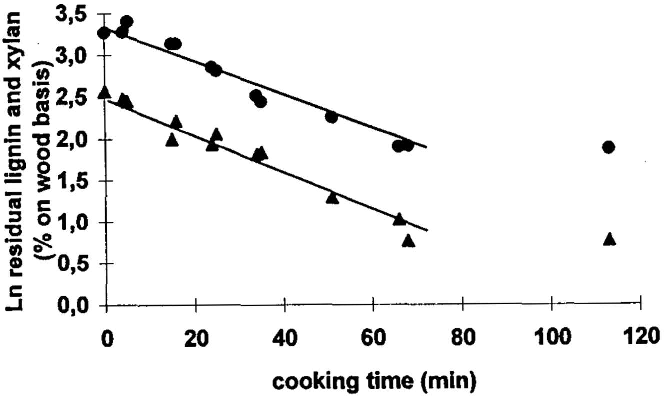

Figure 4. Pseudo-first-order kinetic plots for delignification and xylan removal during organosolv cooking of undecayed *Eucalyptus grandis* wood. Lines represents best fits to simulated points. Black filled points are experimental results. (●) lignin; (▲) xylan.

from bulk to final delignification phase (63 min for the undecayed *E. grandis* sample).

Estimation of Organosolv Pulping Parameters for Fungally Pretreated Samples

The response of fungally pretreated samples to organosolv delignification can be evaluated analyzing the kinetics for solubilization of major wood components during pulping.[7-9] However, the pretreated substrate had its chemical and ultrastructural characteristics changed, owing to the biodegradation process.[9,11,12] As a consequence, fungally pretreated samples can present a different kinetic behavior in organosolv pulping as compared to the undecayed control.

The suitability of the model presented in equation **1** was evaluated for estimating pulping parameters for a set of wood samples previously submitted to biodegradation. Biodegradation pretreatment was performed for periods of 15 days to 4 months with white- and brown-rot fungi: *Punctularia artropurpurascens* and *Wolfiporia cocos*, respectively.[8] The weight and component losses due to biological pretreatment are shown in Table 1. Typical white-rot decay was observed in samples biodegraded by *P. artropurpurascens*, while *W. cocos* promoted brown-rot decay after a period of 30-90 days of biodegradation.[8]

Some decayed samples presented kinetics for pulp yield, as well as, lignin and xylan removal, similar to that observed for the undecayed control. However, in several cases of biotreated samples, wood solubilization kinetics presented an additional phase at the beginning of the process, which was characterized by a very low wood solubilization rate. Including this phase, equation **1** became insufficient for describing the behavior of the pulp yield as a function of the cooking time. This problem was overcome by introducing the term **(1-Y/A)** into equation **1**, resulting in equation **3**.

$$\frac{dY}{dt} = -k_Y Y\left(1-\frac{Y^*}{Y}\right)\left(1-\frac{Y}{A}\right) \qquad (3)$$

Table 1
Wood Weight and Component Losses Caused by White- and Brown- rot Pretreatment

	Weight and component losses (%)			
Fungal Pretreatment	Weight	Glucan	Xylan	Lignin
P. artropurpurascens 15 days	1.5 ± 0.6	0 ± 2	6 ± 2	4 ± 1
P. artropurpurascens 1 month	7.6 ± 0.6	4 ± 4	11 ± 6	14 ± 3
P. artropurpurascens 2 months	9 ± 2	3 ± 2	15 ± 3	16 ± 4
P. artropurpurascens 4 months	12 ± 2	8 ± 2	18 ± 2	20 ± 4
W. cocos 15 days	1.2 ± 0.2	0 ± 0	0 ± 0	5 ± 2
W. cocos 1 month	4.1 ± 0.5	2 ± 2	16 ± 4	5 ± 3
W. cocos 2 months	11 ± 1	10 ± 1	28 ± 3	11 ± 3
W. cocos 4 months	22 ± 3	24 ± 2	29 ± 5	14 ± 3

Parameter **A** is a measure of the length of the initial phase. As A-value increases, the initial phase is shortened. Actually, this model made it possible to predict the kinetic behavior of samples in which no initial phase occurred, since in these cases, **A** approximates to infinite values and equation **3** becomes equation **1**.

The solution of equation **3** satisfying the initial condition $\mathbf{Y} = \mathbf{Y_0}$ at $\mathbf{t} = \mathbf{0}$ is given by equation **4**.

$$\mathbf{Y} = \frac{\left[\dfrac{Y_0 - Y^*}{Y_0 - A}\right] A - Y^* e^{k'_Y t}}{\left[\dfrac{Y_0 - Y^*}{Y_0 - A}\right] - e^{k'_Y t}} \qquad \mathbf{(4)}$$

Parameters $\mathbf{Y^*}$, **A** and $\mathbf{k'_Y} = \dfrac{k_Y(A - Y^*)}{A}$ can be determined by fitting this model to the experimental data. This was also carried out by non-linear regression using the Marquadt's numerical method.[16]

Table 2

Kinetic Parameters of Organosolv Pulping of Undecayed and Fungally Pretreated *Eucalyptus grandis* Wood Samples

Sample	Delignification Rate (10^{-2} min^{-1}) - bulk phase*	Time to change from bulk to final delignification phase (min)**	Xylan Removal Rate (10^{-2} min^{-1}) - bulk phase*	Time to change from bulk to final xylan removal phase (min)**
Control	2.0	63	2.2	65
P. artropurpurascens 15 days	10.7	27	15.2	28
P. artropurpurascens 1 month	6.2	34	8.6	36
P. artropurpurascens 2 months	7.5	33	12.0	34
P. artropurpurascens 4 months	7.0	32	9.4	34
W. cocos 15 days	5.4	43	6.7	44
W. cocos 1 month	5.1	34	6.4	35
W. cocos 2 months	3.8	34	5.1	37
W. cocos 4 months	4.8	33	5.1	34

* Graphically obtained as the slope of best fitted lines from simulated points (see Fig. 4 for an example); ** Intercept of lines obtained from simulated points for each pulping phase.

Table 2 presents the estimated kinetic parameters for the organosolv pulping of fungally pretreated samples. Results show that rate constants of lignin and xylan removal increased for most decayed samples. This increase in delignification rates means that fungally pretreated samples were more easily pulped than the undecayed control, which was expected. This result can be ascribed to chemical and ultrastructural changes that occurred during the biological pretreatment. For white-rotted samples, the delignification rates were higher than for brown-rotted samples, indicating that lignin biodegradation influences the behavior of decayed samples submitted to organosolv pulping. However, there is no clear relationships between lignin losses occurred during biological pretreatment and delignification rates in the organosolv process. This lack of correlation could indicate that the structure of residual biodegraded lignin

Table 3

Estimated Parameters for Mathematical Models Developed for Organososlv Process of White- and Brown-rotted *Eucalyptus grandis* Wood

Sample	Model Type	Model F-value	R^2	Y^*	t-value	A	t-value	K_Y	t-value
control	Equation 2	240.7	0.96	48 ± 4	12.0	----	----	0.026 ± 0.005	5.2
P. artropurpurascens 15 days	Equation 4	53.8	0.94	55 ± 3	18.3	100.01 ± 0.03	3333.7	0.95 ± 0.10	9.5
P. artropurpurascens 1 month	Equation 4	74.8	0.96	56 ± 3	18.7	100.4 ± 0.5	200.8	0.5 ± 0.1	5.0
P. artropurpurascens 2 months	Equation 4	179.6	0.98	60 ± 2	30.0	100.01 ± 0.02	5000.5	0.82 ± 0.07	11.7
P. artropurpurascens 4 months	Equation 4	160.5	0.98	59 ± 2	29.5	100.2 ± 0.2	501.0	0.6 ± 0.1	6.0
W. cocos 15 days	Equation 4	124.7	0.98	58 ± 2	29.0	100.5 ± 0.4	251.3	0.4 ± 0.1	4.6
W. cocos 1 month	Equation 4	74.1	0.96	56 ± 2	28.0	101 ± 2	101.0	0.4 ± 0.1	4.0
W. cocos 2 months	Equation 2	252.4	0.98	52 ± 3	17.3	----	----	0.049 ± 0.007	7.0
W. cocos 4 months	Equation 2	115.2	0.94	47 ± 4	11.8	----	----	0.06 ± 0.01	6.0

should be more important than the extend of lignin removal to increase delignification rates in the organosolv process. More details on this subject can be found in studies by Mendonça *et al.*,[8] Ferraz *et al.*,[9] and continue to be a research area in our laboratories.

Statistical Validity of the Kinetic Parameters and Models

Table 3 shows the estimated parameters of equations **2** and **4**, their standard deviations and t-values. F- and R^2-values for each model are also displayed. Estimated parameters present low standard deviations and in all cases were significant at 99% confidence (high t-values). F-values were also high and models were significant at 99% confidence level. Model predictions agreed well with experimental data resulting in high R^2 values. Moreover, the results obtained show that the structure of the mathematical models developed for describing organosolv pulping kinetics of undecayed samples can be applied to fungally pretreated samples by introducing an additional parameter in the differential equation that describes the pulp yield as a function of the cooking time.

CONCLUSION

Simple mathematical models were developed to describe organosolv pulping kinetics of *E. grandis* wood chips with and without biodegradation pretreatment. The models were used for estimating the rate constants for delignification, xylan removal and for the entire solubilization process. Models were suitable for predicting pulping kinetics for a large group of fungally pretreated samples with different patterns of wood biodegradation. The models proposed will permit further development on the biopulping combined with organosolv delignification for the production of wood pulps.

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