

Hardwood pulping kinetics of bulk and residual phases

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ABSTRACT: The kinetics of the bulk and residual delignification phases of *Eucalyptus nitens*, *E. globulus*, *E. benthamii*, acacia, maple, and loblolly pine were determined in an effort to improve the use of various hardwoods. Kinetic experiments were performed using a microwave digestion system for fast heating of the kraft liquor. Delignification rates were obtained for three different temperatures (150°C, 160°C, and 170°C) and correlated with the wood's syringyl-to-guaiacyl ratio. A linear correlation between the kraft delignification rate and the syringyl-to-guaiacyl ratio was found to exist.

Application: Mills that better understand the kinetics during the different phases of the cooking process can tailor the cooking process to achieve specific desirable outcomes.

The ultimate goal of chemical pulping processes is to remove lignin while retaining carbohydrates in a fibrous form. This goal is only achievable if one has a comprehensive knowledge of raw material and process interactions. Understanding the reaction kinetics of lignin and the carbohydrates during the pulping process assists researchers in establishing reaction conditions that preserve the desirable portions of the starting material while enhancing delignification. As part of this effort, several studies have been performed to try to understand pulping kinetics and their impact on process variables [1-4]. However, few of these studies have looked at both the bulk and residual cooking phases at once for more than one hardwood specie.

Experimental work has suggested that three distinct phases of delignification exist. These are the initial, bulk, and residual phases. Following this three-phase reaction strategy, a kinetic model for kraft delignification of *Eucalyptus globulus* has been proposed. Experimental work and observation of these three reaction phases for *E. globulus* pulping suggest the transition from initial to bulk delignification occurs when 18% of the lignin has been removed (about 82% of the original lignin remaining in the fiber). The bulk-to-residual phase has been found to occur when about 97% of the original lignin has been removed (3% remaining) [1].

In a similar study, Gilarranz et al. proposed a kinetic model for the residual phase of delignification [2]. It was carried out in the temperature range of 150°C-180°C and hydroxide ion concentration range of 0.7-1.6 M. This study found that 95.5% of the original wood lignin was removed at the transition between bulk and residual delignification. The influence of cooking temperature on the rate constant was expressed by an Arrhenius-type equation. A power-law function was employed to model hydroxide ion concentration influence. The

activation energy obtained was 86 kJ/mol, whereas a value of 0.59 was calculated for the kinetic order of the hydroxide ion concentration. The model successfully predicts experimentally obtained values for the wood specie studied. This model is also capable of reproducing delignification trends for other reported experimental studies.

Delignification kinetics of *E. globulus* have been determined in the laboratory using a continuous batch cooking process [5]. The residual lignin was isolated by the dissolved wood lignin method and compared with a conventional acidolysis method. During bulk and residual delignification phases, the syringyl-to-guaiacyl (S/G) ratio of the residual lignin in the fibers continuously decreased while the β -O-4 units and phenolic groups remained almost unaffected, suggesting that the continuous pulping process permits enhanced delignification efficiency and better bleachability.

In another study [6], the residual and dissolved lignins of *E. globulus* were isolated by mild acidolysis and acidic precipitation. The results indicated that during the initial phase of pulping there was preferential removal of guaiacyl (G) and *p*-hydroxyphenyl (H) lignin units covalently bonded with the polysaccharides. During the bulk and residual pulping phases, syringyl (S) lignin units were progressively removed, which led to an increase of the S/G ratio of the dissolved kraft lignin in the black liquor.

Recent studies with 10 different hardwoods and a softwood species have recently been performed to better define lignin and carbohydrate reactions during bulk delignification of kraft pulping [7-9]. Milled wood lignin was isolated from each species and analyzed using quantitative carbon-13 nuclear magnetic resonance spectroscopy, elemental analysis, methoxyl analysis, and nitrobenzene oxidation. The delignification rates of *E. urograndis*, *E. nitens*, *E. globulus*, sweet gum,

maple, red oak, birch, red alder, cottonwood, and acacia were obtained and correlated with their respective lignin chemical structures. The activation energies were calculated for the hardwoods and compared with that of the softwood. A linear correlation between the delignification rate and the amount of S lignin was found. Activation energy values obtained for the hardwoods were very similar to one another and almost identical to the value obtained for the softwood.

Cellulose, xylan, and total carbohydrate bulk phase dissolution kinetics were also determined [8]. A wide range of carbohydrate dissolution rates was obtained for the 10 species studied. Variations in the carbohydrate dissolution rates were correlated to chemical features, such as starting carbohydrate content, lignin S/G ratio, and initial lignin content. It was also determined that carbohydrate dissolution was dependent upon the rate of delignification; that is, species with high carbohydrate dissolution also showed high lignin removal rates.

To better explain the effect of the variations in hardwood lignin structure, such as the S/G ratio, upon the kraft pulping process, we proposed to carry out a similar study to investigate the effect of lignin structure in hardwoods on the transition between the initial and bulk phases and the bulk and residual phases of delignification. Reaction rates for the bulk and residual phases were determined for each of the species studied. Attempts to measure the initial phase kinetics were discontinued due to the lack of useful data obtained after the heating time for the reaction mixtures. All of the reaction rates were measured for lignin. An understanding of the differences between bulk and residual phase reaction rates could be potentially useful for current commercial pulping efforts exploring the impact of stopping the pulping reaction at very high kappa numbers for enhanced yield [10]. It is possible that the differences between bulk and residual phase reactions could be exploited to enhance the cooking methods associated with the high-kappa cooking processes. An understanding of the initial phase reaction rates would also be of interest and should be investigated in future studies [11]. By understanding the similarities and differences of initial, bulk, and residual phase reaction kinetics, it may be possible to improve wood and biomass use for pulping and biorefinery efforts.

EXPERIMENTAL

Raw material

Five different hardwoods species and one softwood specie were obtained from different pulp mills around the world. *Eucalyptus nitens*, *E. globulus*, *E. benthamii*, acacia (*Acacia mangium*), maple (*Acer rubrum*), and loblolly pine (*Pinus taeda*) chips were hand sorted to remove knots and bark. The acceptable chips were ground to pass through a 40-mesh sieve but retained on a 60-mesh sieve. The resulting sawdust was Soxhlet-extracted for 24 h with benzene-ethanol (2:1 [v/v] mixture) in accordance with TAPPI T 264 om-88 "Preparation of wood for chemical analysis." The wood meal samples were placed in capped plastic bottles, and the moisture content was determined for use in the pulping experiments.

Sawdust pulping

Pulping kinetics experiments were performed at 150°C, 160°C, and 170°C and at different cooking times until the residual delignification phase was reached. Pulping times at reaction temperature were 10 min, 15 min, 20 min, 30 min, 40 min, 60 min, 80 min, 100 min, 120 min, and 140 min, depending upon the wood specie and temperature tested. Each experiment also required 10 min to heat the white liquor and wood mixture to the cooking temperature (time-to-temperature). To have a short heating time, the experiments were carried out with a programmable 1200-W microwave digestion system, Milestone Microwave Digestion System Ethos EX (Milestone Inc.; Shelton, CT, USA).

Extractive-free wood meal (3 g) was placed into a 100-mL vessel with a non-stick coating. Each sample was mixed with 30 mL of 25% sulfidity white liquor to obtain a 40% active alkali charge on oven-dry wood. Excess white liquor (liquor-to-wood ratio of 10:1) was used to maintain nearly constant reagent concentrations during the kinetic experiments. For each pulping condition, four vessels were capped and placed symmetrically in the microwave system. Internal temperature and pressure conditions were monitored within one reference vessel equipped with temperature and pressure sensors. The temperature was directly measured from the cooking liquor and controlled according to the programmed temperature profile.

After the desired reaction time, the digester bomb was cooled by running cold water over it for at least 10 min. The samples were removed from the vessels and washed with deionized water until a neutral pH was reached. Pulp yield and lignin content were then determined to calculate the kinetics. The method of Dence and Lin [12] was used to determine the lignin content. Specifically, the Klason lignin content was determined by acid hydrolysis (TAPPI Standard Test Method T 222 om-02 "Acid-insoluble lignin in wood and pulp"). A sample weight of 0.1 g was hydrolyzed with 1.5 mL of 72% sulfuric acid at room temperature with occasional stirring for 2 h. The mixture was then diluted to 3% sulfuric acid using deionized water, transferred to a vial, sealed, and heated to 120°C for 1.5 h. The resulting suspension was filtered, the acid-insoluble residue (Klason lignin) was determined gravimetrically, and the acid-soluble lignin was determined spectrophotometrically using TAPPI UM 250 "Acid-soluble lignin in wood and pulp." The delignification rates were calculated for the bulk and residual phases for all the wood species examined.

RESULTS AND DISCUSSION

Characterization of samples

Table I shows the chemical compositions of the hardwood species and softwood specie used in this study. As expected, pine has the highest total lignin content (33.8%). Among the hardwoods, the total lignin content ranged from 22.3% to 32.3%. Total carbohydrate content for the woods varied from 59.1% to 63.2%, with glucan and xylan as the major sugar com-

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ponents. Pine contains less xylans than the hardwoods, although it contains more mannans and galactans. Glucans comprised 40%-46% of the total wood composition, while xylan varied from 7%-16%. As expected, *E. globulus* is among the species with the highest S/G ratios [13]. The S/G ratio ranged from 0.97-2.73 for the hardwoods employed in this study.

Sawdust delignification

Pulping results for each species, with lignin content and pulp yield for different temperatures, are shown in **Tables II, III, IV, V, VI, and VII**. There was very good correlation between cooking time and percentage of lignin removed for all samples tested. Table II gives pulping results for *E. nitens*. The pulping yield was around 45% and 48%, with the samples reaching

this level faster for 170°C. To obtain yield drops below 50%, at least 60 min of cooking time at temperature was required for the 150°C cooks. Forty minutes of cooking time at temperature was needed to reach yield drops of greater than 50% when operating at 160°C while only 20 min of cooking time at temperature was required for the 170°C cooks. For a total lignin decrease of around 1.5%, at least 30 min of cooking at 170°C, 60 min at 160°C, and 120 min at 150°C were required.

Pulping results for *E. globulus* are shown in Table III. Samples within the same *Eucalyptus* genus showed similar results. The pulping yield was slightly higher, and experiments were performed around 49% and 53% yield. To obtain yield drops below 50%, at least 100 min at cooking temperature of 160°C and 60 min minutes at 170°C were needed. Total lignin was slightly

Species	Lignin (%)			Sugar (%)							S/G Ratio
	Klason	ASL	Total	Ara	Rha	Gal	Glc	Xyl	Man	Total	
<i>E. nitens</i>	17.7	4.6	22.3	0.3	0.4	0.6	41.8	15.9	1.2	60.2	2.59
Acacia	29.9	1.4	31.3	0.5	0.3	0.9	44.3	11.7	1.4	59.1	0.97
Maple	24.0	2.7	26.7	1.0	0.7	0.9	44.7	12.9	1.1	61.3	2.01
<i>P. taeda</i>	33.0	0.8	33.8	2.0	0.1	3.7	40.1	7.3	10.0	63.2	0
<i>E. globulus</i>	18.5	4.3	22.8	0.0	0.0	1.2	46.1	14.0	0.8	62.1	2.73
<i>E. benthamii</i>	28.7	3.6	32.3	0.5	0.6	1.7	44.5	14.4	0.5	62.2	1.85

ASL = acid soluble lignin; Ara = arabinan; Rha = rhamnan; Gal = galactan; Glc = glucan; Xyl = xylan; Man = mannan; S/G = syringyl-to-guaiacyl.

I. Lignin content and sugar composition of the wood species used.

Time (min)	150°C				160°C				170°C			
	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)
	Klason	ASL	Total		Klason	ASL	Total		Klason	ASL	Total	
10	15.5	3.1	18.6	72.1	13.5	3.0	16.5	69.5	10.4	2.7	13.1	65.2
15	—	—	—	—	—	—	—	—	3.4	0.9	4.3	52.0
20	8.5	2.8	11.2	63.2	4.1	1.4	5.4	55.2	1.5	0.6	2.1	48.7
30	5.3	1.9	7.2	58.2	2.7	0.8	3.5	51.4	1.0	0.5	1.6	46.8
40	3.4	1.4	4.8	54.3	2.4	0.5	2.9	47.1	1.1	0.5	1.6	44.9
60	2.8	0.8	3.6	49.6	1.1	0.5	1.6	47.3	1.0	0.3	1.3	45.9
80	1.2	0.6	1.8	48.3	0.9	0.5	1.3	46.4				
100	1.2	0.5	1.7	48.0	0.8	0.5	1.3	48.5				
120	1.1	0.4	1.5	47.9								

*Lignin content based on wood. ASL = acid soluble lignin.

II. Pulping data for *Eucalyptus nitens*.

Time (min)	150°C				160°C				170°C			
	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)
	Klason	ASL	Total		Klason	ASL	Total		Klason	ASL	Total	
10	13.8	4.1	18.0	78.6	14.0	3.7	17.7	73.2	10.0	2.3	12.3	65.4
15	–	–	–	–	–	–	–	–	2.7	0.9	3.5	52.1
20	8.3	2.8	11.1	66.5	3.7	1.5	5.1	58.7	2.3	0.7	3.0	51.9
30	6.8	1.8	8.6	60.3	2.4	0.8	3.2	53.8	0.6	0.5	1.1	50.4
40	5.0	1.5	6.5	58.0	1.2	0.6	1.8	51.6	0.5	0.5	1.0	51.1
60	2.4	0.8	3.3	53.7	0.6	0.5	1.1	51.5	0.5	0.4	0.9	48.7
80	0.6	0.6	1.2	52.9	0.5	0.5	1.0	50.1	0.5	0.3	0.8	48.3
100	0.6	0.5	1.0	52.9	0.4	0.5	0.9	49.3				
120	0.7	0.4	1.1	51.3	0.5	0.3	0.9	47.0				

*Lignin content based on wood. ASL = acid soluble lignin.

III. Pulping data for *Eucalyptus globulus*.

Time (min)	150°C				160°C				170°C			
	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)
	Klason	ASL	Total		Klason	ASL	Total		Klason	ASL	Total	
10	15.2	2.4	17.6	71.0	16.3	2.5	18.8	69.2	9.8	1.7	11.5	56.4
15	12.7	2.0	14.7	63.8	–	–	–	–	8.7	1.5	10.2	54.7
20	11.6	1.9	13.5	61.8	8.3	1.5	9.8	53.5	6.0	0.6	6.7	50.4
30	11.3	1.8	13.2	62.4	4.4	1.0	5.4	47.8	0.9	0.4	1.4	41.3
40	10.1	1.7	11.8	59.3	0.9	0.6	1.5	41.7	0.5	0.4	0.9	40.1
60	5.7	1.1	6.7	51.3	0.5	0.5	1.0	40.7	0.5	0.4	0.9	39.5
80	1.4	0.7	2.1	43.6	0.6	0.3	0.9	38.7	0.5	0.4	0.9	38.6
100	0.8	0.4	1.2	42.3	0.5	0.4	0.8	40.2	0.5	0.3	0.8	39.5
120	1.1	0.4	1.5	41.8								
140	0.7	0.4	1.1	41.2								

*Lignin content based on wood. ASL = acid soluble lignin.

IV. Pulping data for *Eucalyptus benthamii*.

lower than *E. nitens* and dropped to around 1.0% for all temperatures. Cooking times to reach this delignification level for the various temperatures were similar to that of *E. nitens*.

Pulping results for *E. benthamii* are shown in Table IV. Delignification levels were similar to *E. globulus*, and 1.0% total lignin levels were obtained for all cooking temperatures. To reach this level of delignification, it took at least 40 min at 170°C, 60 min at 160°C, and over 120 min at 150°C. Final yields

for *E. benthamii* were the lowest among samples tested and ranged from 39%-42%. Pulp yields decreased below 50% after 30 min of cooking at 170°C and 160°C and 80 min at 150°C.

Pulping results for acacia are shown in Table V. This wood specie afforded the highest pulp yield values among the wood samples tested, with values over 50% for all temperatures. Yield ranged from 52% (160°C and 170°C) to 60% (150°C). This yield difference could be explained because lignin con-

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Time (min)	150°C				160°C				170°C			
	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)
	Klason	ASL	Total		Klason	ASL	Total		Klason	ASL	Total	
10	20.2	1.1	21.3	77.3	16.9	0.9	17.8	70.8	17.9	1.0	18.9	72.3
15	–	–	–	–	–	–	–	–	11.0	0.8	11.8	60.0
20	17.0	0.9	17.8	70.2	14.2	0.8	15.0	68.5	8.8	0.7	9.6	60.9
30	16.4	1.0	17.4	71.6	12.9	0.9	13.8	67.5	5.8	0.6	6.4	58.4
40	13.4	1.0	14.4	68.7	11.4	0.7	12.1	63.0	5.5	0.5	6.0	53.1
60	10.6	1.0	11.5	64.2	5.3	0.5	5.8	54.2	2.1	0.4	2.5	52.2
80	8.6	0.8	9.3	60.0	4.2	0.6	4.8	53.8	2.0	0.3	2.3	51.3
100	6.8	0.7	7.5	59.4	4.4	0.5	4.9	53.4				
120	3.3	0.6	3.9	59.1								

*Lignin content based on wood. ASL = acid soluble lignin.

V. Pulping data for acacia.

Time (min)	150°C				160°C				170°C			
	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)
	Klason	ASL	Total		Klason	ASL	Total		Klason	ASL	Total	
10	15.8	1.9	17.7	73.3	12.0	1.5	13.5	66.2	9.9	1.5	11.3	64.0
15	–	–	–	–	–	–	–	–	7.3	1.1	8.5	46.3
20	8.4	1.2	9.7	63.3	4.5	0.8	5.3	55.2	2.6	0.7	3.3	49.9
30	8.1	1.2	9.3	62.6	2.8	0.7	3.5	54.1	1.8	0.6	2.4	48.3
40	5.2	1.0	6.2	58.5	2.3	0.4	2.7	52.8	1.8	0.4	2.3	48.0
60	3.0	0.5	3.5	50.8	2.1	0.4	2.5	51.4	1.2	0.4	1.6	49.3
80	2.9	0.7	3.6	53.7	1.3	0.5	1.8	50.5				
100	2.0	0.5	2.5	49.9								

*Lignin content based on wood. ASL = acid soluble lignin.

VI. Pulping data for maple.

tent for 150°C was still dropping and did not level off even after 120 min of cooking. The lignin content stabilized around 2.4% for the 170°C cooks after 60 min at temperature. About 80 min at temperature was required for the 160°C cooks to drop the lignin content to 4.8%. These times to obtain lignin losses were the longest among hardwood samples examined.

Pulping results for maple are shown in Table VI. Among the samples tested, the lignin content decreased and reached a plateau level faster. Residual lignin ranged from 1.6%-2.5%, and only 30 min at 170°C was required to remove lignin below 3%, 10 min less than at 160°C. For 150°C, 100 min was re-

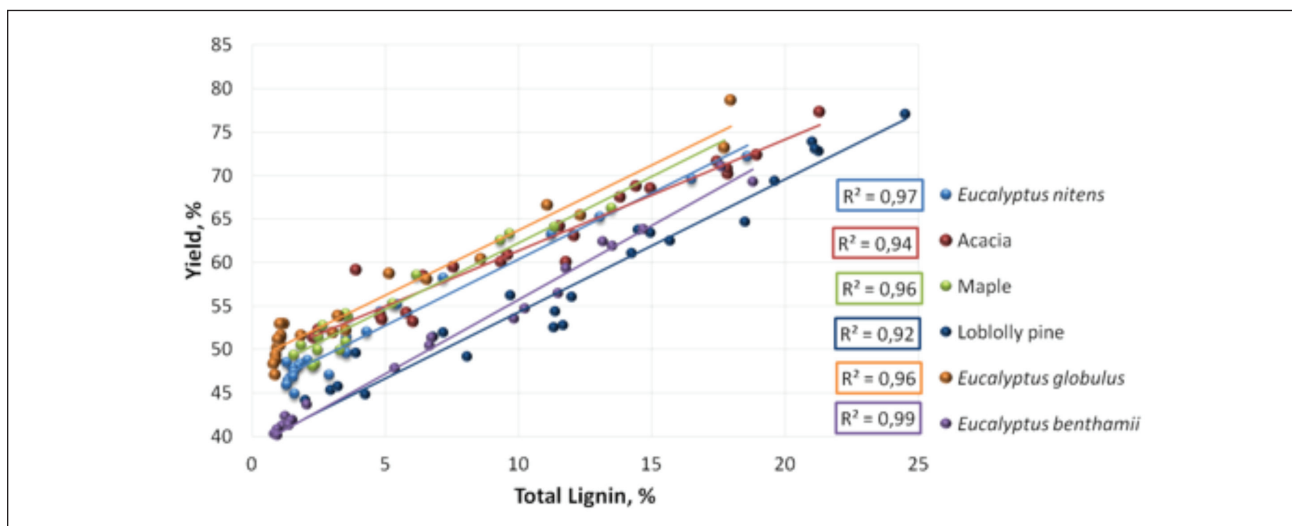
quired to obtain the same delignification level. Yield ranged from 48%-50% for most samples.

Pulping results for loblolly pine are shown in Table VII. As expected, pine pulp yields were lower than most of the hardwood pulp yields, ranging from 41%-45%. Also, longer cooking times were required to obtain adequate levels of delignification for the pine versus the hardwoods. Lignin content leveled off at 8% after 120 min of pulping at 150°C. At 160°C and 170°C, lignin content dropped to 2.9% and 2.0%, respectively, but did not level off over the times examined at these temperatures.

Time (min)	150°C				160°C				170°C			
	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)	Lignin (%)*			Yield (%)
	Klason	ASL	Total		Klason	ASL	Total		Klason	ASL	Total	
10	24.2	0.3	24.5	77.1	20.7	0.3	21.0	73.9	20.8	0.4	21.1	73.0
20	21.0	0.2	21.3	72.7	14.7	0.2	14.9	63.3	13.9	0.3	14.2	61.1
30	19.3	0.3	19.6	69.3	14.1	0.4	14.5	63.7	11.4	0.2	11.7	52.7
40	18.1	0.4	18.5	64.6	11.8	0.2	12.0	56.0	10.9	0.4	11.3	52.5
60	15.3	0.4	15.7	62.4	9.3	0.4	9.7	56.2	4.0	0.2	4.3	44.8
80	11.0	0.4	11.4	54.3	6.6	0.2	6.8	51.4	3.0	0.2	3.2	45.7
100	7.7	0.3	8.1	49.2	3.5	0.3	3.9	49.6	1.8	0.2	2.0	44.1
120	6.8	0.4	7.2	51.9	2.8	0.2	2.9	45.3				
140	7.5	0.3	7.8	41.4								

*Lignin content based on wood. ASL = acid soluble lignin.

VII. Pulping data for loblolly pine.



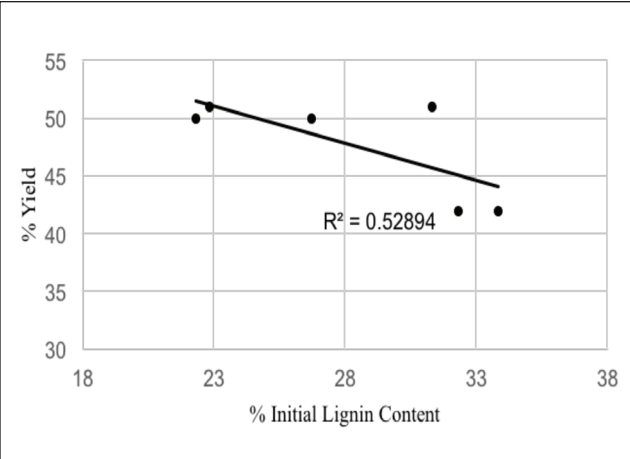
1. Sawdust pulping selectivity curves at all temperatures (150°C, 160°C, and 170°C).

Unfortunately, the kraft delignification process is accompanied with alkali hydrolysis of the carbohydrates, which results in pulp yield loss. Thus, minimization of the carbohydrate losses during delignification is a major objective to evaluate a satisfactory pulping technology. Pulping selectivity was plotted in **Fig. 1** using the pulping yield versus total lignin data to represent selectivity. A linear correlation was determined to fit the data reasonably well.

It is known that lignin and yield decrease as temperature increases, but the correlation among yield loss and lignin content did not change with different pulping temperatures. All species tested showed the same selectivity rate. No correlation was found between cooking temperature and pulping selectivity, probably because these experiments were done

	Total Initial Lignin, %	S/G Ratio	Yield at 5% Lignin	Yield at 2.5% Lignin
<i>Eucalyptus nitens</i>	22.3	2.59	52	50
Acacia	31.3	0.97	55	51
Maple	26.7	2.01	54	50
<i>P. taeda</i>	33.8	0	46	42
<i>Eucalyptus globulus</i>	22.8	2.73	57	51
<i>Eucalyptus benthamii</i>	32.3	1.85	47	42
S/G = syringyl-to-guayacil.				

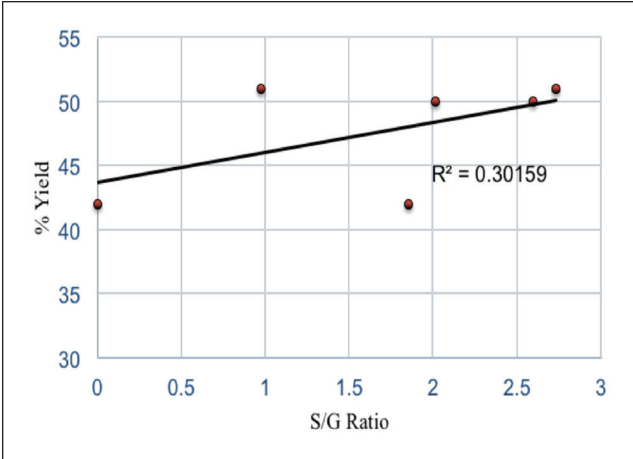
VIII. Yield at a constant lignin content.



2. Percent yield at 2.5% lignin as a function of the initial lignin content.

with excess alkali and the effect of temperature on pulp yield is masked. Also, as shown by Gustafson et al. [14] and Santos et al. [8] during kinetics studies, carbohydrate degradation and lignin removal are linearly related. As lignin is removed, carbohydrates are also linearly removed but at a slower rate. The yield at constant lignin content is shown in **Table VIII** for both 5% and 2.5% lignin. An effort to correlate the yield showed that the yield had better correlation with the initial lignin content than the S/G ratio, as shown in **Figs. 2 and 3**. As expected, the higher initial lignin content pulps exhibited lower pulp yields.

The kinetic experiments were conducted with an excessive alkali charge as an attempt to maintain nearly constant alkali charge during the pulping experiments. By maintaining the alkali charge constant, pseudo-first-order reaction kinetics could be assumed with respect to lignin content. The delignification rate constant was calculated from the slope of a plot of the natural log of the residual lignin divided by the original lignin content ($\ln[L/L_0]$) versus reaction time. Three distinct linear segments exist in this plot corresponding to the initial, bulk, and residual phases of delignification. Pseudo-first-order reaction rates were found to provide good ex-



3. Percent yield at 2.5% lignin as a function of the syringyl-to-guaiacyl ratio.

perimental fits for the bulk and residual phases for each species studied. The pseudo-first-order fit is in good agreement with similar studies [4,7,15]. As the initial phase segment consisted of only the initial lignin and the 10 min at temperature data point, these data were determined to be insufficient for kinetic rate determination.

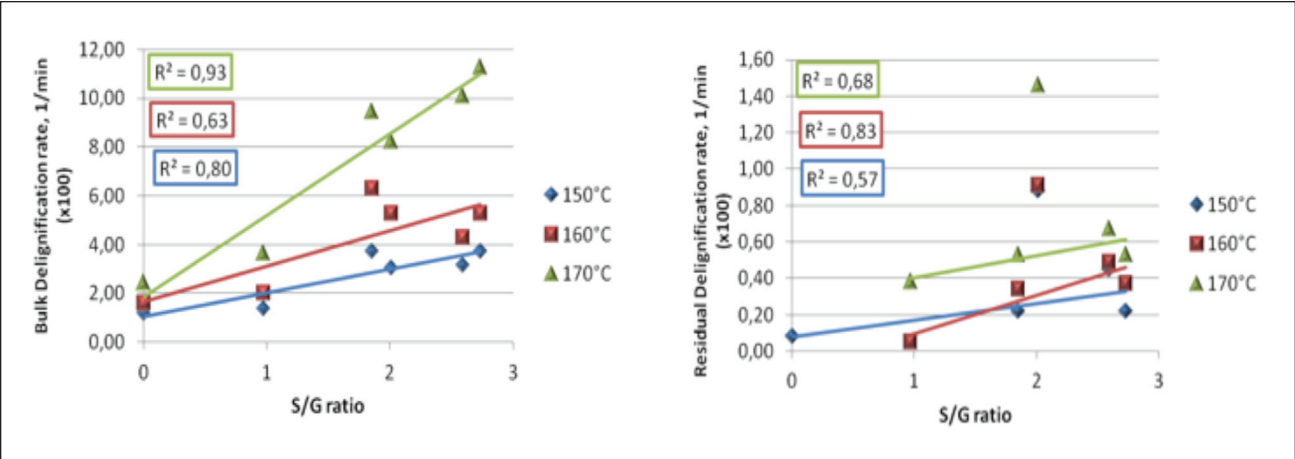
Delignification rate constants for the bulk and residual phases for the different temperatures studied are shown in **Table IX**. The residual phase of delignification was not reached for all samples (e.g., for acacia at 150°C and pine at 160°C and 170°C).

The initial cooking period is characterized by rapid delignification and rapid consumption of alkali. It occurs during the impregnation phase, below 140°C. It was difficult to discern a definitive initial phase for the hardwoods, and it is possible that delignification proceeds into the bulk phase very quickly during delignification. Due to experimental limitations, the initial phase of delignification was not calculated (first point of reaction was obtained only after 10 min). The second slope was used for the bulk phase determination and the last slope for the residual phase. Most of the lignin is removed in the bulk phase and the transition

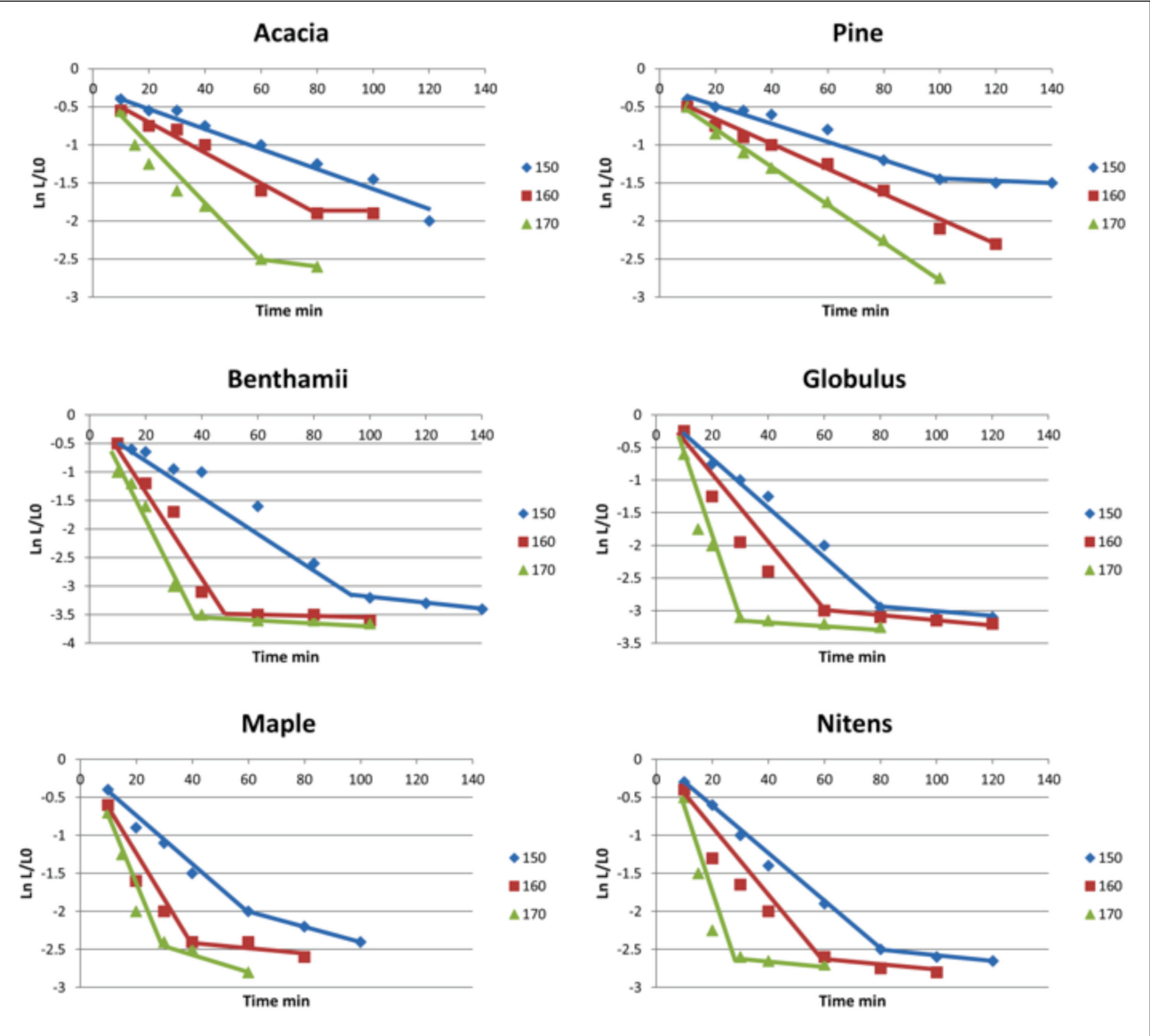
	Temperature, °C	<i>E. globulus</i>	<i>E. nitens</i>	Acacia	Maple	Pine	<i>E. benthamii</i>
Bulk Phase	150	3.71	3.14	1.38	3.05	1.17	3.71
	160	5.28	4.29	2.02	5.28	1.60	6.31
	170	11.25	10.1	3.66	8.23	2.44	9.44
Residual Phase	150	0.22	0.45	—*	0.88	0.08	0.22
	160	0.37	0.49	0.05	0.91	—	0.34
	170	0.53	0.67	0.38	1.46	—	0.53

* — = not obtained.

IX. Delignification rate constant, 1/min (x 100).



4. Bulk and residual delignification rate versus syringyl-to-guaiacyl ratio for acacia.



5. Residual lignin (L/L_0) for all the species.

	Total Lignin, %	S/G Ratio	% of Original Lignin Content at Transition from Bulk to Residual Phase, (L/L ₀) 150°C	% of Original Lignin Content at Transition from Bulk to Residual Phase, (L/L ₀) 160°C	% of Original Lignin Content at Transition from Bulk to Residual Phase, (L/L ₀) 170°C
Pine	33.8	0	7.2	NA*	NA
<i>E. nitens</i>	22.3	2.59	1.8	1.6	1
Acacia	31.3	0.97	NA	4.8	2.5
Maple	26.7	2.01	3.5	2.7	2.4
<i>E. globulus</i>	22.8	2.73	1.2	1.1	1.1
<i>E. benthamii</i>	32.3	1.85	1.2	1	0.9
* NA = residual phase not achieved. S/G = syringyl-to-guayacil.					

X. Lignin content at the transition from bulk to residual phase.

from bulk to residual phase may vary from 2.5% to 1.1% lignin on wood [3,18]. The residual phase is characterized by very slow delignification, significant carbohydrate degradation, and significant alkali consumption.

A wide range of reaction rate constants were obtained. A high rate constant represents a higher delignification rate and therefore a more reactive lignin. The majority of kraft delignification reactions occur during the bulk phase of cooking, and higher temperature represents the highest rates. Values for residual rates were very low. In general, eucalyptus species presented the highest bulk delignification rates, whereas acacia and pine presented the lowest rates.

The delignification rates change significantly with the specie and conditions used in the initial period [4,16]. Differences in the kinetics may be accounted for with the wood chemistry for each species. To explain the differences between species, the delignification rates were correlated with wood S/G ratios. As shown in **Fig. 4**, very good correlations between S/G and delignification rates were found for the bulk and residual phases. Even though it was not possible to calculate the initial phase reaction rates, it is known that a significant amount of alkali consumption and xylan cleavage occurs as a zero-order reaction at the beginning of a cook and that no correlation should exist between the initial phase delignification rate and the S/G ratio [11,17]. As S lignin increases, condensed lignin structure decreases and β -O-4 linkages increase. The delignification rate constant increases with higher S/G ratio and with higher temperatures. These findings are very important and confirm the benefits of S/G ratio for the kraft process [18].

As shown in **Fig. 4**, only acacia had an unexpected behavior during residual delignification. Acacia residual rates were the highest while S/G ratio did not follow it, most likely due to the limited number of data points available for rate calculation. More work needs to be performed to better understand the

reaction kinetics associated with this species.

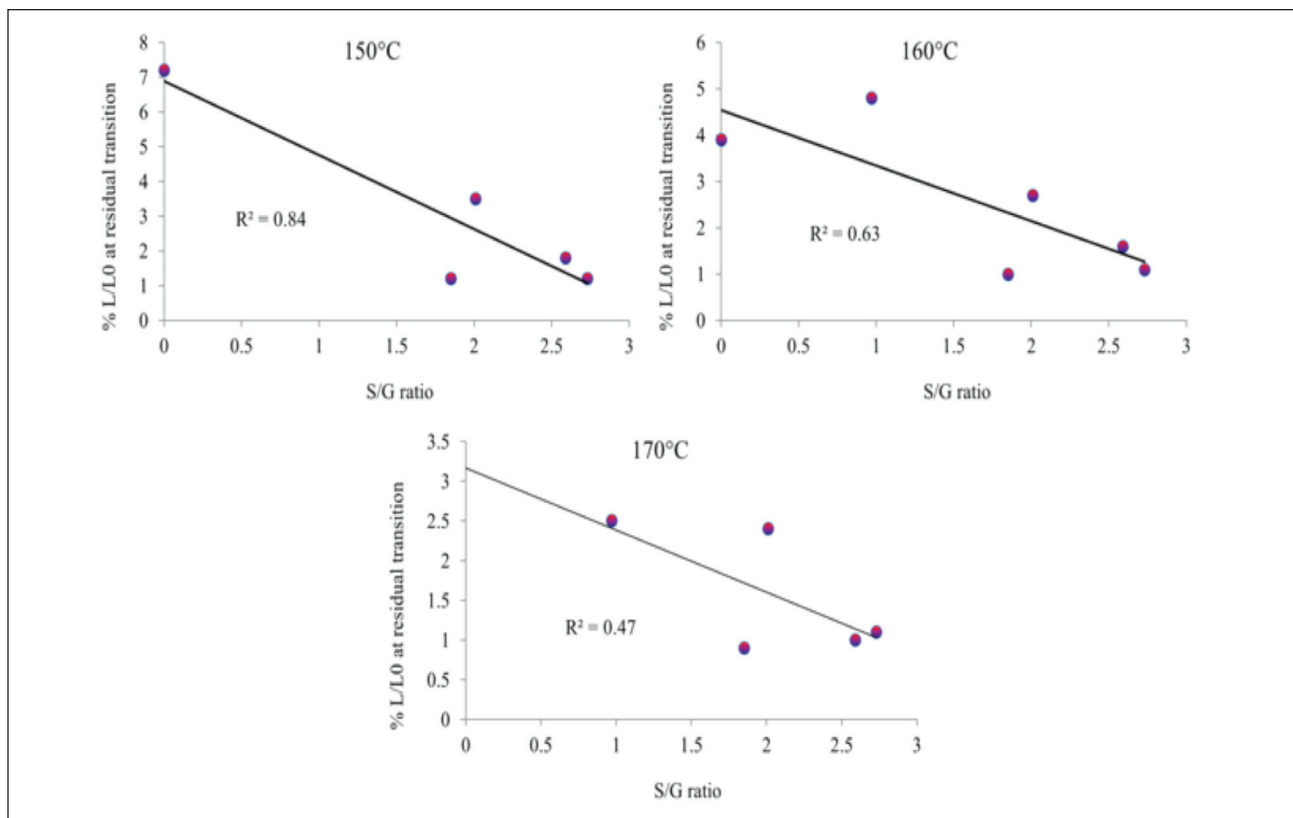
The residual lignin content is the lignin content where the kinetics change from bulk delignification to residual delignification. Residual lignin has significance for pulping because it also represents the amount of lignin that is more difficult to remove during pulping. The logarithmic analysis to determine bulk-to-residual phase transition is shown in **Fig. 5**, and the residual lignin content for each of the species at the transition point is shown in **Table X**. The L/L₀ for the species studied varied depending on the species and the pulping temperature. Higher temperatures resulted in lower lignin content at the start of the residual phase. This implies that if a lower kappa number is desired, it would be beneficial to pulp at higher temperatures. Further studies are needed to better understand the overall impact of cooking temperature and bulk to residual transition point on kappa number and yield. **Figure 6** shows the residual lignin as a function of the S/G ratio. The lower L/L₀ at high S/G ratio implies that it may be possible to pulp to low kappa numbers using hardwoods with high S/G ratios, thereby decreasing the cost of bleaching.

CONCLUSIONS

The overall yield at a constant kappa number was affected more by the initial lignin content than the S/G ratio. Temperature did not have a significant impact on pulping selectivity.

A wide range of delignification rate constants were obtained for the various species. These variations indicate how easy or difficult the delignification process will be for each species. Eucalyptus species were established as the easiest to delignify.

Delignification rate constants increase with temperature at the three phases. Eucalyptus had the highest syringyl content when compared to the other species. A linear correlation was found to exist between delignification rates in the bulk and



6. Residual lignin content at bulk-to-residual phase transition as function of syringyl-to-guaiacyl ratio.

residual phases and the S/G ratio. For the residual phase, more experimental data points are needed to better understand this behavior. Some of the acacia and pine samples did not successfully reach the residual pulping phase in the current study.

The residual lignin content was affected by both the pulping temperature and the S/G ratio. This observation is important as we try to achieve lower kappa number in the pulping process to minimize bleaching cost and environmental impacts. In the future it would be important to study these species with changing alkali profile to reflect realistic pulping conditions. **TJ**

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ABOUT THE AUTHORS

Recent efforts to extend pulping yield by stopping the cooking process at high to very high kappa numbers have resulted in a need to better understand the kinetics during the early and bulk phases of cooking. It has also become important to understand the differences between these cooking phases and the residual delignification phase of cooking.

Our work was an attempt to determine cooking conditions earlier in the cook. We used a microwave cooking process to reduce the heating time required, which allowed us to look at the cooking process after only 10 min of heating time.

We were initially attempting to look at all three phases of the cooking process. Our biggest challenge was that even with a rapid 10 min heating process, we were not able to fully elucidate the initial phase kinetics. We have not fully decided how to best determine the initial phase kinetics, and further efforts are required in this area.

Better understanding of the kinetics during the different phases of the cooking process will allow



Almeida



Santos



Hart

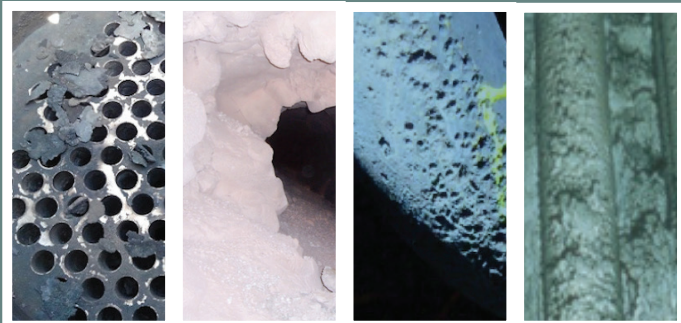


Jameel

mills to tailor the cooking process for specific desirable outcomes. The next step is to develop technically solid methods of determining the initial phase kinetics.

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