Hardwood Kraft Pulping Kinetics

Diego Almeida: PostDoctoral, UFV, Brazil, diego.almeida@ufv.br
Hasan Jameel: Full Professor, NCSU, USA, jameel@ncsu.edu
Peter Hart: MeadWestvaco Corporation, USA, peter.hart@mwv.com
Ricardo Santos: MeadWestvaco Corporation, USA, ricardo.santos@mwv.com

Abstract

In an attempt to improve the utilization of different hardwood species, this study analyzed the kinetics of initial, bulk and residual delignification phases of *Eucalyptus nitens, E. globulus, E. benthamii,* acacia, maple and Loblolly pine. Kinetics experiments were performed using a Microwave Digestion System model Milestone Ethos EX 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 wood lignin S/G ratio. Activation energy values were also calculated and they appear to have a linear correlation with wood S/G ratio. It was also found a linear correlation between the Kraft delignification rate and the S/G ratio. This study can provide a better understand of semi-chemical and low kappa pulping process and also bioconversion industry, identifying opportunities for optimizing raw materials selection based on delignification behavior.

Keywords: Hardwood, Kinetics, delignification phases.

Introduction

Removal of lignin with carbohydrates preservation is the ultimate goal of any pulping process. This can only be achievable if a comprehensive knowledge of raw material and process interactions is understood. This makes the understanding of lignin and carbohydrates pulping kinetics of great interest for better raw material and process utilization.

Lignin kinetics of *Eucalyptus globulus* has been done using continuous batch cooking pulp [1]. The residual lignin was isolated by dissolved wood lignin (DWL) protocol and compared with conventional acidolysis protocol. During bulk and residual delignification, the S/G ratio of lignin remaining in the fibers continuously decreased, while the β-O-4 units and phenolic OH groups remained almost unaffected, suggesting that the continuous process permits enhanced delignification efficiency and good bleachability.

Few authors have studied hardwood pulping kinetics and some of them have focused at just one species. A kinetic model for the kraft pulping delignification of *Eucalyptus globulus* was proposed and initial, bulk, and residual delignification stages have been observed during the lignin removal, the transitions being, referring to the lignin initial content, about 82 and 3% [2].

A recent study with 10 different hardwoods and one softwood was done [3, 4 and 5] to explain lignin and carbohydrate reactions during bulk delignification of kraft pulping. Milled wood lignin (MWL) was isolated from each species and analyzed using quantitative 13C NMR spectroscopy, elemental analysis, methoxyl analysis and nitrobenzene oxidation. The kraft pulping delignification rate of *E. urograndis, E.nitens, E.globulus*, sweet gum, maple, red oak, birch, red alder, cottonwood and acacia was obtained and correlated with their respective lignin chemical structures. The activation energy (Ea) was calculated for hardwood and compared with softwood activation energy. A linear correlation between the kraft delignification rate and the amount of syringyl was found. Activation energy values obtained for kraft pulping of hardwoods were very similar and almost identical to the value obtained for softwood.

In order to better explain the effect of hardwood lignin structure during the kraft pulping process, it was proposed to carry out a similar study to investigate the effect of lignin structure in hardwoods on the initial phase of delignification and compare the results to bulk and residual phases. Both reaction rates and activation energy for the initial and residual phase were measured for the different hardwood species and loblolly pine. The reaction rates were measured for lignin. An understanding of the initial phase is critical for semi-chemical pulping processes and also for the overall pulping reactions. This study aim to provide a better understand of low kappa pulping process and also bioconversion industry, identifying opportunities for optimum raw materials selection based on delignification behavior.

Experimental

To perform this study was used five different hardwoods and one softwood specie that were received as wood chips from different pulp and paper mills. *Eucalyptus nitens*, *Eucalyptus globulus*, *Eucalyptus 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 a 40-mesh sieve and retained on a 60-mesh sieve. Before pulping and compositions analysis, the resulting sawdust was Soxhlet-extracted for 24h with benzene-ethanol 2:1 (v/v) in accordance with TAPPI T 264 om-88 "Preparation of wood for chemical analysis". The wood meal samples were placed in plastic bottles and the moisture determined.

Pulping kinetics experiments were performed at 150°C, 160°C and 170°C and different cooking time until residual delignification phase was reached. Pulping times were 10, 15, 20, 30, 40, 60, 80, 100, 120 and 140 min, depending on wood species and temperature tested. The first 10 min for each pulping condition was used to heat the white liquor (TTT-time to temperature). In order to have a short heating time for white liquor, this experiment was carried out with a programmable 1200 W microwave digestion system (Milestone Microwave Digestion System Ethos EX). The Ethos system is unique because it makes use of microwave energy to heat the system which shortens TTT.

Each vessel was mixed with 30 mL of 25% sulfidity white liquor. Excess white liquor (liquor: wood ratio of 10:1) was used to maintain nearly constant reagent concentrations during the kinetic experiments. Therefore, the active alkaline charge was 40% based on oven dry wood. For each pulping condition, four vessels were capped, and placed symmetrically in the microwave system. The temperature was directly measured in the sample solution, and was always the controlling parameter of the digestion program.

After the desired reaction time, the whole apparatus was cooled by running cold water through it for at least 10 min. The samples were removed from the vessels and washed with deionized water until a neutral pH was reached. Cooking yield and lignin content [6] were then determined for kinetics calculations. The kraft pulping delignification rate and the activation energy were calculated for the initial, bulk and residual phase for all the different species.

The Klason lignin was determined by acid hydrolysis [7]. A sample weight of 0.1 g was hydrolyzed with 1.5 mL of 72% sulfuric acid room temperature with occasional stirring for 2h. The mixture was then diluted to 3% sulfuric acid using deionized water, transferred to a vial, sealed, and heated to 120°C for 1.5h. The resulting suspension was filtered, the acid-insoluble residue (Klason lignin) was determined gravimetrically and the acid-soluble lignin was determined spectrophotometrically [8].

Results and discussion

Table I brings the chemical characterization of hardwoods and softwood species used. As expected, pine has the highest lignin content, 33.8%. Among the hardwoods, the lignin ranged from 22.3% to 32.3%. Total carbohydrate content varied from 59.1% to 63.2% with glucan and xylan as major components. Pine contain less xylan than the hardwoods, although contains more mannans and galactans. Glucans composed 40% to 46% of the total wood composition, while xylan varied from 7% to 16%. As expected, *E globulus* is among the species the highest S/G ratio [9], ranging from 0.97 to 2.73 for hardwoods.

Table I. Lignin Content and Sugar Composition

Species	Lignin, %			Sugar, %							S/G ratio
	Klason	ASL	Total	Ara	Rha	Gal	Glc	Xyl	Man	Total	
E. nitens	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
L. Pine	33.0	0.8	33.8	2.0	0.1	3.7	40.1	7.3	10.0	63.2	-
E. globulus	18.5	4.3	22.8	0.0	0.0	1.2	46.1	14.0	0.8	62.1	2.73
E. benthamii	28.7	3.6	32.3	0.5	0.6	1.7	44.5	14.4	0.5	62.2	1.85

Pulping results for each species, with lignin content and yield for different temperatures are shown at Tables II, III, IV, V, VI and VII. There was a very good correlation between cooking time and percentage of lignin removal during the kinetics for all samples tested. Table II gives wood meal pulping results for *E. nitens*.

The final yield established around 45% and 48%, getting this level faster for 170°C. To the yield drops below 50%, was used at least 60 minutes of cooking at 150°C, 40 minutes at 160°C and 20 minutes at 170°C. Total lignin dropped around 1.5% for all temperatures, and for this was used at least 30 minutes of cooking at 170°C, 30 minutes less than the time used for 160°C and 50 minutes less than 150°C. Cooking time was extended to 120 minutes for 150°C while was needed to the same delignification degree only a half of this time for 170°C.

Table II. Pulping Data for *Eucalyptus nitens*

Time	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

Pulping results for *E. globulus* are shown at Table III. As samples within the same genus, *E. globulus* and *E. nitens* showed similar results. Globulus final yield was slightly higher and established around 49% and 53%. To the yield drops below 50%, was used at least 100 minutes of cooking at 160°C and 60 minutes at 170°C. Total lignin was slightly lower than *E. nitens* and dropped around 1.0% for all temperatures. Cooking time to get this delignification level was the same used for nitens. Cooking time was extended to 120 minutes for 150°C, 120 minutes for 160°C and 80 minutes for 170°C.

Table III. Pulping Data for *Eucalyptus globulus*

Time	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

Other eucalyptus tested was *E. benthamii* and pulping results are shown at Table IV. Total lignin was similar with *E. globulus* and dropped around 1.0% for all temperatures, and for this was used at least 40 minutes of cooking at 170°C, 20 minutes less than the time used for 160°C and 60 minutes less than 150°C.

Final yield results are the lowest among samples tested, and it ranged from 39% to 42%.Yield drops below 50% after 30 minutes of cooking at 170°C and 160°C, and 80 minutes at 150°C. Cooking time was extended to 140 minutes for 150°C, 100 minutes for 160°C and 100 minutes for 170°C.

Table IV. Pulping Data for *Eucalyptus benthamii*

Time	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

Pulping results for acacia are shown at Table V. This wood sample gave the highest final yield values among the samples tested, 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 content for 150°C is still dropping and did not establish even after 120 minutes of cooking. Lignin established around 2.4% for 170°C after 60 minutes of cooking, and for 160°C, was used 20 minutes more until lignin drops to 4.8%. These times to establish lignin losses were the longest among hardwood samples. Cooking time was extended to 100 minutes for 160°C and to 80 minutes for 170°C.

Table V. Pulping Data for Acacia

Time	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

Table VI gives wood meal pulping results for maple. Among samples tested, the lignin content dropped and established faster. Last total time used was 100 minutes for 170°C, 80 minutes for 160°C and 60 minutes for 150°C. Residual lignin ranged from 1.6% to 2.5% and was used only 30 minutes at 170°C to remove lignin below 3%, 10 minutes less than 160°C. For 150°C was used 100 minutes for the same delignification level. Yield ranged from 48% to 50% as most of samples. After 15 minutes of cooking, yield for 170°C was below 50%, while the same level for 150°C used 100 minutes.

Table VI. Pulping Data for Maple

	150°C				160°C				170°C			
Time	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

In order to compare with hardwood results, loblolly pine pulping results are shown at Table VII. As expected, pine yield results are lower than most of hardwood yield, and it ranged from 41% to 45%. Also comparing with hardwood, were used longer cooking times. Lignin established at 8% after 120 minutes for 150°C. At 160°C and 170°C lignin dropped to 2.9% and 2.0% respectively, but did not establish, even after 120 and 100 minutes.

Table VII. Pulping Data for Loblolly Pine

	150°C				160°C				170°C			
Time	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

Unavoidable, the delignification process is accompanied with carbohydrate hydrolysis. Thus, reduction of carbohydrate loss during lignin removal is the focus of any satisfactory pulping technology. Pulping selectivity was plotted at Figure 1 using the pulping yield versus total lignin with a linear correlation. Pulping selectivity rate is given by the slope of the straight line. Perfect selectivity would occur with the minimum rate 1, so higher slope means lower selective process. As expected, hardwood selectivity lines are shifted up compared with pine, because it has higher yield contend. With similar yield, *E. benthamii* line was also shifted down.

It is known that lignin and yield decrease as temperature increases, but the correlation between yield loss and lignin content does not change with different temperatures. All species tested showed the same selectivity rate. It was not found any correlation between temperature of cooking and pulping selectivity.

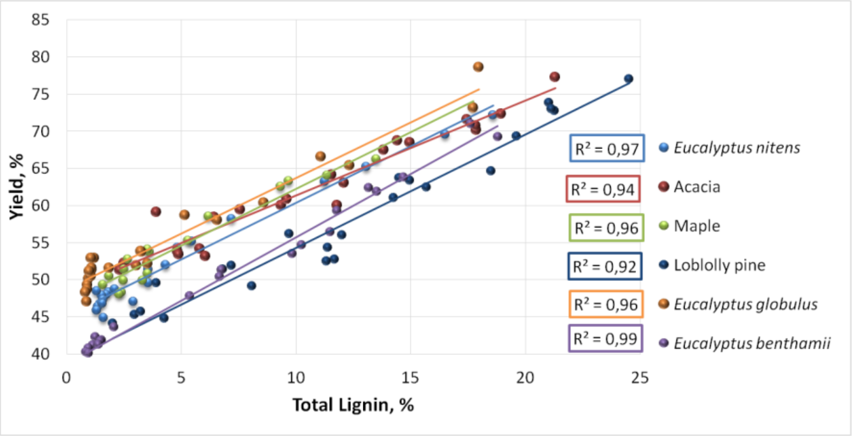

Figure 1. Sawdust Pulping Selectivity curves

As polymers such carbohydrates and extractives consume part of the alkaline solution, an excess in alkali charge was necessary in order to isolate those reactions that made it possible to conduct the experiment without their interference. The delignification rate constant value was calculated using the slope of a linear function plotted using the ln of original lignin and residual lignin ($\ln L/L_0$) ratio versus reaction time. This plot shows three different slopes, initial, bulk and residual phases of delignification. Each species studied presented a pseudo-first order reaction, in agreement with similar studies [10, 11 and 12].

Sawdust delignification constant for initial, bulk and residual phase for different temperature are shown at Table IX. The residual phase of delignification was not reached for all samples, as for acacia at 150°C and pine at 160°C and 170°C.

Table IX. Sawdust Delignification Rate Constant (X100)

	Temperature	*E. globulus*	*E. nitens*	Acacia	Maple	Pine	*E. benthamii*
Initial Phase	150 °C	2.38	1.83	3.85	4.11	3.21	6.08
	160 °C	2.53	3.02	5.63	6.82	4.76	5.43
	170 °C	6.16	5.35	5.03	8.56	4.70	10.36
Bulk Phase	150 °C	3.71	3.14	1.38	3.05	1.17	3.71
	160 °C	5.28	4.29	2.02	5.28	1.60	6.31
	170 °C	11.25	10.1	3.66	8.23	2.44	9.44
Residual Phase	150 °C	0.22	0.45	-	0.88	0.08	0.22
	160 °C	0.37	0.49	0.05	0.91	-	0.34
	170 °C	0.53	0.67	0.38	1.46	-	0.53

- : not detected

The initial phase is characterized by rapid delignification and large alkali consumption. It occurs at impregnation phase, below 140°C. The transition from initial to bulk period in Kraft process takes place at a lignin content of about 22% on wood [13]. The initial phase of delignification was calculated using the first point of reaction, at 10 minutes (TTT). The second slope was used for bulk phase and last slope for residual phase of delignification. Most of the lignin is removed in bulk period and the transition from bulk to residual period may vary from 2.5% to 1.1% on wood [11 and 14]. The residual period 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 the Kraft delignification reaction occurs during the bulk phase of cooking and higher temperature represents higher rates. In general the initial rates were higher than bulk rates. It does not apply for *E. globulus* and *E. nitens*. Values for residual rates were very low. In general, eucalyptus species presented the highest bulk delignification rates and the lowest value was obtained for acacia.

The delignification rates changes significantly with the specie and conditions used in the initial period [10and 15]. Differences in the kinetics may be accounted with the wood chemistry for each species. In order to explain the differences of species delignification rates, it was correlated with wood S/G ratio. At bulk and residual phases were found a very good correlation with S/G ratio, as shown at Figure 2. Initial delignification phase did not present any correlation with S/G ratio. As syringyl lignin increases, condensed lignin structure decreases and β-O-4 linkages increase. These findings are very important and confirm the benefits of S/G ratio for kraft process [12]. Rate of delignification increases with higher lignin S/G ratio and with higher temperatures.

As showed at Figure 2, only acacia had an unexpected behavior during residual delignification. Acacia residual rates were the highest while S/G ratio did not follow it. Further work for this species will be done as future work.

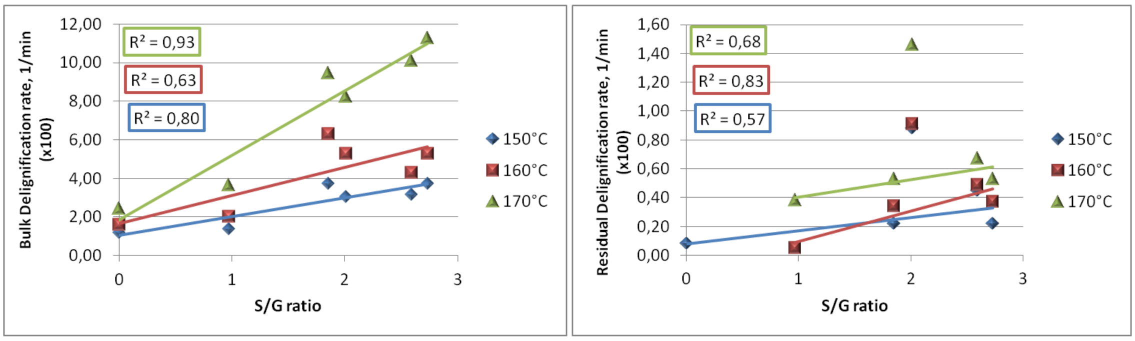

Figure 2. Bulk and Residual Delignification Rate vs S/G Ratio

Activation energy (Ea) defines the energy that must be overcome in order for a chemical reaction to occur. It was calculated based on rearranged Arrhenius equation. This equation gives the quantitative basis of the relationship between the activation energy and the rate at which a reaction proceeds. From the Arrhenius equation, the activation energy can be expressed as:

$$k = Ae^{-Ea/RT} \quad (1)$$

where A is the frequency factor for the reaction, R is the universal gas constant, T is the temperature (in Kelvin), and k is the reaction rate coefficient.

It was used the Arrhenius plot, taking the natural logarithm of Arrhenius' equation:

$$ln(k) = \frac{Ea}{R}\frac{1}{T} + ln(k) \quad (2)$$

Equation (2) has the same form as an equation for a straight line, Y = ax+b. So, when a reaction has a rate constant that obeys Arrhenius' equation, a plot of ln (k) versus T^{-1} gives a straight line, whose gradient and intercept can be used to determine E_a. This procedure has become common to define the activation energy for a reaction. That is the activation energy is defined to be (-R) times the slope of a plot of ln(k) vs. (1/T)

A kinetics experiment [12] for some hardwood species and activation energy for bulk phase of the kraft pulping process presented almost the same value for hardwood and softwood. Activation energy for the three phases of delignification were calculated and is shown at Table X.

Table X. Activation Energy Values for Delignification Phases, KJ/mol

	E. globulus	*E. nitens*	Acacia	Maple	Pine	*E. benthamii*
Initial	74	84	21	57	30	41
Bulk	86	91	76	77	57	73
Residual	69	31	-	39	-	68

Different activation energy values were found and correlated with wood S/G ratio. A straight line with very good correlation was found for initial and bulk phases of delignification (Figures 3). Activation energy for residual phase could not be calculated for all species as was not reached all delignification rates. Any correlation was found for residual phase.

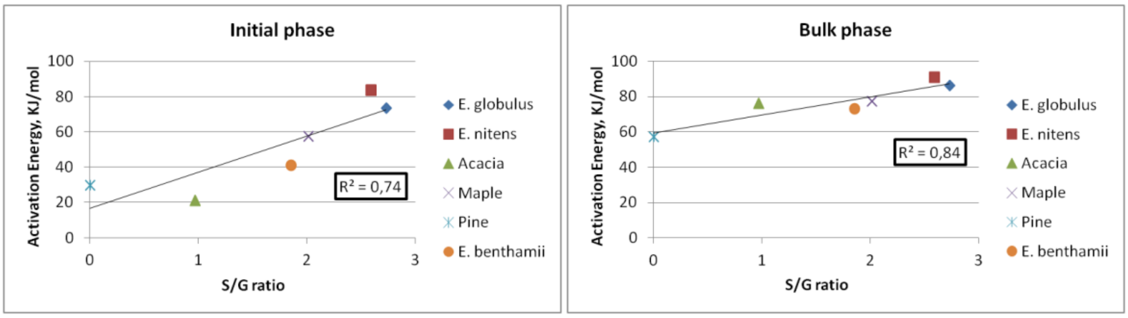

Figure 3. Initial and Bulk Activation Energy vs S/G Ratio

The H factor is determined using the procedure proposed by Vroom [16], known as Vroom's H factor model which provides a method for expressing both cooking time and temperature as a single numerical variable. Further Vroom assumed activation energy for softwood of the order 134 kJ/mol to create the model by rearranging Arrhenius equation.

$$\text{Vroom's H Factor [16]: } H = \int_0^t e^{-Ea / RT(t)}\, dt$$

The H factor is based on the assumption that delignification is a single reaction. While this model holds well, lignin is not actually a “pure” compound undergoing a single chemical reaction to achieve delignification. Rather lignin is a complex molecule which participates for many types of reactions occurring during the delignification process.

Mathematical model is important to analyze, and correlate the system behavior. Besides, it can help to control and optimize the process. No mathematical model for different hardwood species has been done. Different H factor models can be made using the correct values of E_a to help and optimize pulp and paper industries.

Conclusions

1. Delignification rates constant increase with temperature at the three phases. *Eucalyptus* had the highest syringyl content when compared to the other species. A linear correlation was found when delignification rates were correlated with S/G ratio.
2. Were found no differences among pulping selectivity for the three temperatures tested neither among wood samples using the yield vs. lignin plot.
3. The activation energy for each species and each delignification phase were calculated. Different values were found among the species, but they were function of S/G ratio.

References

1. Rutkowska E.W., Wollboldt, P., Zuckerstätter, G., Weber, H.K. and Sixta, H., Characterization of Structural Changes in Lignin During Continuous Batch Kraft Cooking of *Eucaliptus globulus, BioResource* 4(1), 172-193 (2009).
2. Santos, A., Rodríguez, F., Gilarranz, M.A., Moreno, D. and García-Ochoa, F., Kinetic Modeling of Kraft Delignification of *Eucalyptus globulus, Ind. Eng. Chem. Res*. 36(10): 4114 (1997).
3. Santos, R.B., Capanema, E.A., Balakshin, M.Y., Chang, H.M. and Jameel, H., Effect of Hardwoods Characteristics on Kraft Pulping Process: Emphasis on Lignin Structure, *BioResources,* 6(4): 3623 (2011).

4. Santos, R.B., Jameel, H., Chang, H.M. and Hart, P.W., Kinetics of Hardwood Carbohydrate Degradation During Kraft Pulp Cooking, *Ind. Eng. Chem. Res*. 51: 12192 (2012).
5. Santos, R.B., Jameel, H., Chang, H.M. and Hart, P.W., Impact of Lignin and Carbohydrate Chemical Structures on Kraft Pulping Process and Biofuel Production, *Tappi Journal,* Vol. 12, No. 7 (2013).
6. Dence, C.W. and Lin, S.V., Methods of Lignin Chemistry, Springer-Verlag, Berlin, Germany (1992).
7. TAPPI T 222 om-02, Acid-insoluble lignin in wood and pulp, in: 2002-2003 TAPPI Test Methods (2002).
8. TAPPI UM 250, Acid-soluble lignin in wood and pulp, in: 1991 TAPPI Useful Methods, (1991).
9. Magaton, A.S., Oliveira, R., Lopes, O.R., Milagres, F.R., Veloso, D.P. and Colodette, J.L., Composição Quimica da Madeira de Espécies de Eucalipto, *29ª Reunião Anual da Sociedade Brasileira Química*, SQB (2006).
10. Wilder, H.D. and Daleski, E.J., Delignification rate studies. Part II of a series on kraft pulping kinetics, *Tappi* 48 (5), 293-297 (1965).
11. Kleinert, T.N., Mechanisms of alkaline delignification I. The overall reactionpattern, *Tappi* 49(2), 53-57 (1966).
12. Santos, R.B., Capanema, E.A., Balakshin, M.Y., Chang, H.M. and Jameel, H., Lignin structural variation in hardwood species, *Proceedings of the 16th ISWFPC* (2011).
13. Gustafson, R.R., Sleicher, C.A., McKean, W.T. and Finlayson, B.A, Theoretical Model of the Kraft Pulping Process, *Ind. Eng. Chem. Process Des. Dev.* Vol. 22, No. 1 (1983).
14. Rekunen, S., Jutila, E., Lahteenmaki, E., Lonnberg, B., Virkola, N. E., Examination of Reaction Kinetics in Kraft Cooking. *Pap Puu*, 62(2) (1980).
15. Lemon, S., Teder, A., Svensk Papperstidn, 76, 407 (1973).
16. Vroom, K.E., The H Factor: the means of expressing cooking times and temperatures as a single variable. *Pulp and Paper Magazine of Canada,* 58(3) 228-31 (1957)

Acknowledgments

The authors are grateful to Federal University of Viçosa and North Carolina State University. Funding provided by the Minas Gerais State Research Foundation (FAPEMIG), from the Brazilian National Council for Science and Technology Development (CNPq), from the Coordination for the Improvement of Higher Education Personnel (CAPES) and MeadWestvaco Corporation (MWV) is greatly appreciated.