Impact of lignin and carbohydrate chemical structures on kraft pulping processes and biofuel production

RICARDO B. SANTOS, HASAN JAMEEL, HOU-MIN CHANG, AND PETER W. HART

ABSTRACT: Most studies aimed at determining rates of hardwood delignification and carbohydrate degradation have focused on understanding the behavior of a single wood species. Such studies tend to determine either the delignification rate or the rate of carbohydrate degradation without examining the potential interactions resulting from related variables. The current study provides a comprehensive evaluation of lignin and carbohydrate degradation during kraft pulping of multiple hardwood species. The kraft delignification rates of *Eucalyptus urograndis, E. nitens, E. globulus*, sweet gum, maple, red oak, red alder, cottonwood, and acacia were obtained. The kinetics of glucan, xylan, and total carbohydrate dissolution during the bulk phase of the kraft pulping process for those species also were investigated. The wide ranges of delignification and carbohydrate degradation rates were correlated to wood chemical characteristics. It appears that the syringyl:guaiacyl lignin ratio and lignin-carbohydrate complexes are the main factors responsible for the differences in kraft pulping performance among the hardwoods studied.

Application: The results of this study can help mills identify opportunities for optimum raw materials selection for various conversion processes.

Kraft pulping is the dominant chemical process used to produce fibers for papermaking. The use of sodium hydroxide and sodium sulfide (the active cooking chemicals in the kraft process, known as white liquor) brings a number of advantages when compared with other processes, especially in terms of fiber strength. Disadvantages are also present, especially the loss in pulp yield caused by carbohydrate instability (dissolution, peeling, and degradation during the alkaline reaction). To minimize such losses, it is important to have a good and reliable understanding of the chemical process and the raw materials used in the cook. Interactions between process conditions and raw materials also might require special attention.

During the kraft pulping process, white liquor promotes lignin dissolution and fiber liberation. The kraft pulping process goes through three distinct phases as the wood chips are cooked into pulp: the initial phase, the bulk phase, and the residual phase. Significant amounts of carbohydrates are lost during the initial phase as a result of dissolution and in the bulk and residual phases as a result of degradation. The bulk phase is known to promote from 60% to 68% of the total delignification of the wood [1,2]. Less harsh process conditions can result from wood containing easily removed lignin, which leads to carbohydrate preservation.

When comparing wood delignification and process conditions, it is important to note that softwood species are generally harder to pulp than hardwoods. Softwood native lignin appears to vary little between species [3,4], and therefore, fewer improvements in the process (related to wood) can be achieved. On the other hand, there is increasing evidence that the structure of hardwood native lignin varies greatly between species. The major difference in hardwoods is the presence of syringyl (S) and guaiacyl (G) lignin units within the same wood species. Different hardwood species have been found to have differing S:G ratios, which allows for the opportunity to improve process conditions. A more suitable native lignin might allow for a reduced alkali charge, lower cooking temperature, or decreased retention time. Because these conditions result in milder cooking conditions, an increase in pulp yield and fiber quality may be expected [5,6].

Considerable variation in kraft pulping performance of different hardwood species has been reported [7-10]. A study with model compounds showed indications that the β-aryl ether linkage of syringyl lignin is cleaved much more easily than that of guaiacyl lignin [11]. Because β-O-4 is a dominant structure in lignin and appears to highly correlate with the S:G ratio, there have been many studies that have investigated the effect of the S:G ratio on kraft pulping of hardwoods [7-10,12,13]. Even within the same species of *Eucalyptus globulus* wood, evidence of the influence of the S:G ratio on pulp yield and ease of pulping has been reported, leading to

the inclusion of lignin S:G ratio as a selection parameter in clonal breeding programs for pulpwood production [9,14]. Similar results also were reported for various clones of *E. grandis* and the *E. grandis* × *E. urophylla* hybrid [15,16]. The correlation between ease of pulping and the S:G ratio was not as strong in other studies, leading to the suggestion that lignin structural features other than the S:G ratio also might play a role in delignification reactions [16]. At least one study has suggested that the stereochemistry associated with the β-O-4 ether linkage might play an important role in delignification reactions as well [4].

As with delignification, three different reaction steps are known to result in the degradation of carbohydrates during kraft pulping: initiation, peeling (beta-elimination), and end-group stabilization reactions (termination or stopping reactions). The extent of carbohydrate degradation for each of these steps depends on the different reactivity of their chemical and supramolecular composition [17].

Acetyl groups from xylan and galactoglucommannans are readily hydrolyzed at the beginning of the cook. Carbohydrate yield loss occurs mainly as a result of extensive degradation of hemicelluloses, which have a low degree of polymerization and a significant percentage of amorphous regions. The presence of methyl-uronic acid groups tends to stabilize xylan end groups and reduce the amount of alkaline peeling that occurs during the cooking process [18,19]. Cellulose is relatively resistant to kraft pulping liquor (white liquor).

Carbohydrate degradation of softwood has been the focus of many studies, and such research has yielded a variety of kinetic equations with different degrees of complexity. In general, kinetic models that start with wood chips and focus on the dissolution of the wood components have produced models that better represent industrial practice.

When it comes to the modeling of hardwood kinetics, fewer studies are available. Most of the studies dealing with hardwood have focused on the understanding of carbohydrate-lignin behavior of a single wood species [20,21]. Most studies also tend to determine the activation energies associated with the three different cooking phases and for the different reactions that participate in carbohydrate degradation. Additionally, hardwood studies have mainly been conducted in a more superficial manner than the softwood studies.

The activation energy for total carbohydrates has being reported to be 220 kJ/mol for alkaline hydrolysis reactions [22]. In the same study, Giudici et al. found a much lower number for the activation energy associated with end-group stabilization (55 kJ/mol) and peeling reactions (68 kJ/mol). In a study where the authors [23] divided the total carbohydrates into two components (cellulose and hemicellulose) it was found that the activation energy for dissolution of cellulose is higher than the activation energy for hemicellulose, independent of the cooking phase. Cellulose dissolution exhibited an activation energy value of 125 kJ/mol in the initial phase, while the hemicellulose activation energy was only 50 kJ/mol. In the residual phase, the cellulose dissolution activation energy was determined to be 160 kJ/mol, while that of hemicellulose was only 118 kJ/mol. In a fairly comprehensive study involving kinetic modeling of both softwood and hardwood, Johansson [24] found that degradation of xylan and cellulose from softwood is negatively affected by high concentrations of hydroxide, hydrogen sulfide, and sodium ions.

In this work, a comprehensive study of both lignin and carbohydrate degradation during kraft pulping has been performed and results were correlated to the species chemical features (lignin content and structure and carbohydrates content) of *Eucalyptus urograndis*, *E. nitens*, *E. globulus*, sweet gum, maple, red oak, red alder, cottonwood, and acacia. The influence of differing wood species on biofuel production also was investigated.

MATERIALS END METHODS

Raw material

Samples of *E. nitens*, *E. globulus*, *E. urograndis*, sweet gum (*Liquidambar styraciflua*), red maple (*Acer rubrum*), red oak (*Quercus rubra*), red alder (*Alnus rubra*), cottonwood (*Populus trichocarpa*), acacia (*Acacia mangium*), and loblolly pine (*Pinus taeda*) were obtained from different pulp and paper mills around the world. The chips were hand sorted to remove knots and bark. The sorted, acceptable chip samples were ground and sieved. The resulting wood meals (40-60 mesh) were Soxhlet-extracted for 24 h with benzene-ethanol 2:1 (v/v) in accordance with TAPPI T 264 om-88 "Preparation of wood for chemical analysis," dried, and used for pulping and lignin isolation.

Sawdust delignification, carbohydrates degradation rate constant, and kraft pretreatment

Carbohydrates degradation experiments were performed at 150ºC using *E. nitens*, *E. globulus*, *E.urograndis*, sweet gum, maple, red oak, red alder, cottonwood, acacia, aspen, and loblolly pine. Stainless steel autoclaves (50 mL) were filled with 3 g of ovendry extracted wood meal plus 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% on ovendry wood. The autoclaves were closed and placed into the laboratory digester. White liquor with the same ionic concentration was circulated from the digester through an external heater and back into the digester to heat the 50 mL autoclaves placed inside the digester. This procedure was used to ensure the same heat transfer properties inside the autoclaves and the fluid heating them, which is controlled by the digester. After the desired reaction time, the whole apparatus was cooled by running cold water through it. The samples were removed from the bombs and washed with deionized water until a neutral pH was reached. Cooking yield and lignin content [25] were then determined for kinetics calculations. Kinetics experiments also were used as pretreatments for enzymatic hydrolysis.

Enzymatic hydrolysis

One gram (dry weight) of pretreated sample was subjected to enzymatic hydrolysis. The samples were placed into a 50 mL centrifuge tube with enough buffer solution (pH 4.8) to bring the consistency to 5%. Three commercial enzymes were used: cellulase (*Trichoderma reesei*, NS-50013), xylanase (*Aspergillus oryzae*, NS-50014), and *β*-glucosidase (*Aspergillus niger*, NS-50010). Cellulase was added at a dose of 20 filter paper units/g of substrate. Xylanase and *β*-glucosidase were dosed at 30% of the weight of the cellulose solution charged [26]. The tubes were placed in an incubator shaker (180 rpm) for 48 h at a temperature of 50±2°C (122±3.6°F).

After incubation was completed, the samples were filtered using medium porosity glass crucibles and the residue washed one time with buffer solution and two times with deionized water. The solutions were then combined for carbohydrate analysis. The residue was dried (105°C [221°F]) for weight loss evaluation and compositional analysis.

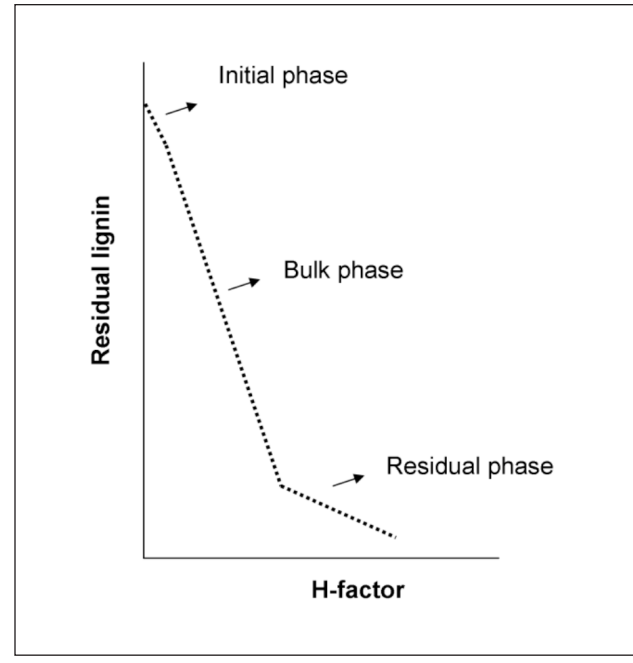
Carbohydrate analysis

The samples' carbohydrate composition was determined by acid hydrolysis [27]. A sample weight of 0.1 g was hydrolyzed with 1.5 mL of 72% sulfuric acid 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 (248°F) for 1.5 h. The resulting suspension was filtered, and the filtrate was analyzed for monomeric sugar units. Fucose was added as an internal standard.

The monomeric sugar content was determined by injecting 2.5 mL samples into a high-performance anion-exchange chromatography column with pulsed amperometric detection on an ion chromatography system. Sugars were separated using a guard unit to prevent contamination and analytical columns were connected in series. Water was used as the eluent at a flow rate of 1.0 mL/min. The column temperature was 18°C. A post-column base of 40 mM sodium hydroxide was added to improve detection by pulsed amperometry. The post-column flow rate was 1.0 mL/min.

^{13}C-NMR for lignin structure quantification

Carbon-13 nuclear magnetic resonance (^{13}C-NMR) analysis was performed according to the method of Capanema et al. [28]. ^{13}C-NMR spectra of the lignin preparations in dimethyl sulfoxide d-6 (DMSO-d6) were recorded on a 300 MHz spectrometer at 300 K (27°C) using a 90° pulse width, a 1.4 s acquisition time, and 1.7 s relaxation delay. Milled wood lignin (MWL) was isolated according to the modified protocol of Capanema et al. [28], where all samples were extracted with 0.3% sodium hydroxide for 1 h to remove tannins. The ball-milled wood was extracted with 96% aqueous *p*-dioxane, in accordance with the method of Bjorkman [29]. The targeted milled wood lignin yield was 27%. Chromium (III) acetylacetonate (0.01 M) was added to the lignin solution to provide complete relaxation of all nuclei. A total of 20000 scans were collected.



1. The three cooking phases.

RESULTS AND DISCUSSION

Kraft cooking kinetics

The majority of the kraft delignification reaction occurs during the bulk phase of cooking. Therefore, the kinetics experiments were designed to investigate the effect of the bulk reaction cooking phase on delignification and carbohydrate degradation (**Fig. 1**). Polymers such as carbohydrates and extractives consume part of the alkaline solution; therefore, an excess of alkali charge was necessary to isolate those reactions and maintain a constant alkali concentration during the bulk delignification reaction phase. Rates were measured at 150°C for four different periods (20, 30, 45, and 60 min).

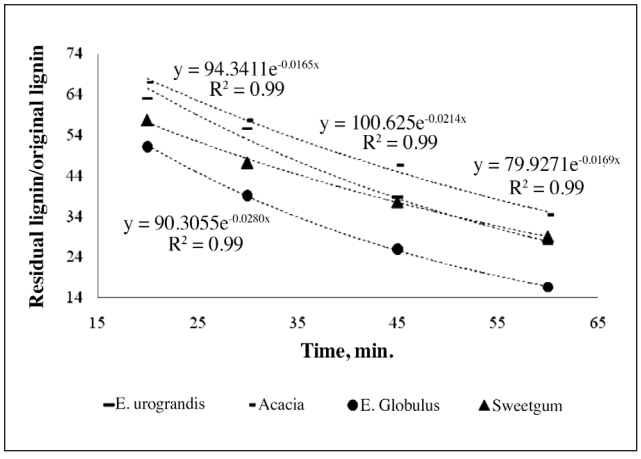
All species studied presented a pseudo-first order reaction for delignification and carbohydrate degradation. Pseudo-first order reactions were found to be in good agreement with previous studies [17,30-32].

The degradation rate constant values were determined by best fitting these data to an exponential function. As a result, the first-order kinetic rate equation could be written as shown in Eq. (1):

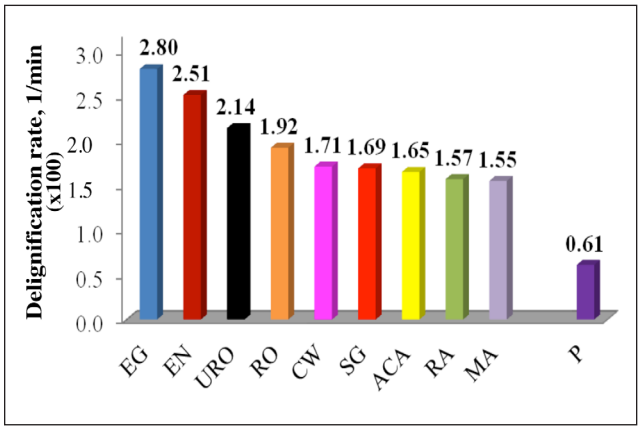
$$dC/dt = k' [C] \quad (1)$$

where C is the ratio of residual lignin or carbohydrate being examined and k' is the pseudo first order rate constant. The value of k' was determined graphically from the experimental data by plotting C/C_o *100% as a function of time and fitting the data using standard kinetic techniques [12,27].

Figure 2 shows examples of how the rates were obtained. Rates were calculated using the exponential equation shown in each curve.



2. Rate constants from exponential equations.



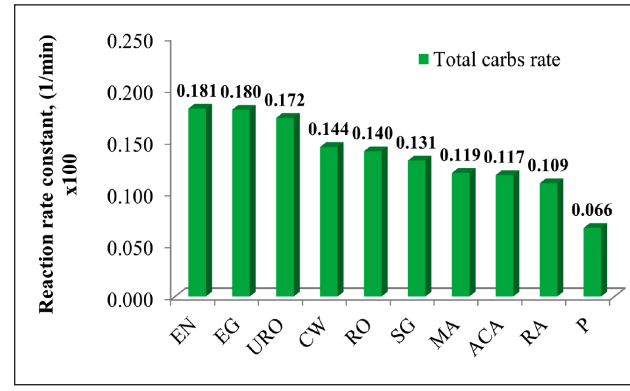
3. Delignification rates for **Eucalyptus nitens** *(EN),* **E. globulus** *(EG),* **E. urograndis** *(URO), sweet gum (SG), red maple (MA), red oak (RO), red alder (RA), cottonwood (CW), acacia (ACA), and loblolly pine (P).*

Delignification rate constant

A wide range of reaction rate constants were obtained for the various hardwoods examined (**Fig. 3**). A high rate constant represents a higher delignification rate and therefore a more reactive lignin. In general, eucalyptus species presented the highest delignification rates. The highest values were assigned for *E. globulus*, followed by *E. nitens*, and *E. urograndis*. The lowest value was obtained for maple wood. Figure 3 can be divided into three different zones: The first zone contains species that are easily delignified (e.g., eucalypts), the second zone is composed of species (from red oak to acacia) that have moderate delignification rates, and the third zone contains species (e.g., red alder and maple) that have low delignification rates. The softwood rate of delignification was less than half the values observed for hardwoods with low delignification rates (e.g., maple). These rates show and verify the general belief that hardwoods pulp far more easily than softwoods. The relative standard deviation for the experiments was 2.1%.

Species	Degradation rates, (1/min) x 100		
	Glucan rate	Xylan rate	Total carbs rate
EG	0.156	0.300	0.180
EN	0.124	0.250	0.181
URO	0.136	0.245	0.172
RO	0.094	0.240	0.140
SG	0.116	0.230	0.131
MA	0.105	0.198	0.119
CW	0.070	0.167	0.144
ACA	0.096	0.162	0.117
RA	0.141	0.144	0.109
P	0.055	0.130	0.066

I. Glucan and xylan degradation rates for **Eucalyptus nitens** *(EN),* **E. globulus** *(EG),* **E. urograndis** *(URO), sweet gum (SG), red maple (MA), red oak (RO), red alder (RA), cottonwood (CW), acacia (ACA), and loblolly pine (P).*



4. Total carbohydrates degradation rates for **Eucalyptus nitens** *(EN),* **E. globulus** *(EG),* **E. urograndis** *(URO), sweet gum (SG), red maple (MA), red oak (RO), red alder (RA), cottonwood (CW), acacia (ACA), and loblolly pine (P).*

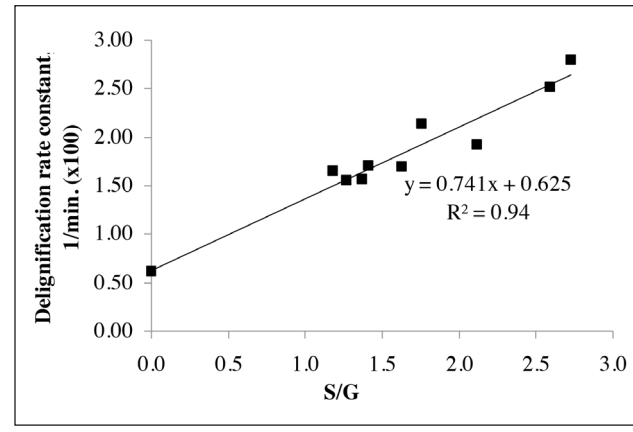
Carbohydrates degradation rate constants

Similar to the delignification experiments, a broad collection of carbohydrate degradation reaction rate constants were obtained for the different hardwoods examined (**Table I** and **Fig. 4**). Degradation reaction rates were determined for glucans, xylans, and total carbohydrates for each of the hardwood species studied. A high rate constant represents increased carbohydrate degradation, and therefore, higher yield loss at a specific reaction time. In general, the eucalypt species had the highest degradation rates, especially for xylan and total carbohydrates. The highest degradation rate constant values were obtained for *E. globulus*, followed by *E.nitens* and *E.urograndis*. The lowest value was obtained for red alder. Glucan degradation rates were more constant than xylan rates among all the hardwood species studied, and lower than their xylan degradation rates (Table I). In general,

hemicelluloses are more easily degraded under alkaline conditions than cellulose because of their low degree of polymerization and lower degree of crystallinity (more amorphous regions) [33]. The relative standard deviation for the experiments was 2.6%.

Impact of lignin structure

To explain differences in the rate of delignification among the different species, the species' carbohydrate (glucan, xylan, and total carbohydrate) and lignin contents were determined. Additionally, lignin structures were obtained from ^{13}C-NMR (see: Santos et al. [34] for complete NMR characterization), and fiber morphologies were correlated with the rate constant values. Other than lignin structure, no other chemical or morphological [35] feature appears to affect delignification or carbohydrates degradation rates.



5. Delignification ratio as a function of syringyl:guaiacyl lignin ratio.

Relationship between wood delignification and lignin structure

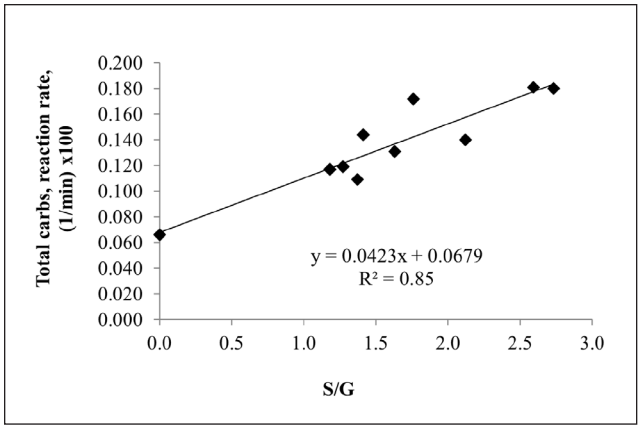
Table II shows the main lignin structures quantified on hardwood species. A substantial variation in syringyl and guaiacyl content among the species was found, and those values strongly correlated with the delignification rate constant. As shown in **Fig. 5**, a straight line was found ($R^2 = 0.94$), indicating a high influence of syringyl lignin on the kraft pulping delignification process. As syringyl lignin increases, condensed lignin structure decreases and β-O-4 linkages increase [35]. These findings are very important and confirm the benefits of a high S:G ratio for the kraft process. Moreover, the use of species with high syringyl lignin content may reduce alkali consumption requirements, and consequently, decrease fiber degradation, resulting in increased fiber strength. Species having high S:G ratio also can be suitable for cellulosic bioethanol processes that have an alkaline stage as pretreatment. When used as a pretreatment stage for a bioethanol process, it is desirable to remove lignin to render the cellulose more accessible to enzymatic attack. An alkaline pretreatment stage can be used for hemicellulose removal and for opening wood structures. Depending on the pretreatment extent and type of treatment applied, it is possible to use alkaline conditions in a pretreatment. More details on wood species influence on cellulosic ethanol production are presented later in this manuscript.

Relationship between carbohydrate dissolution and lignin structure

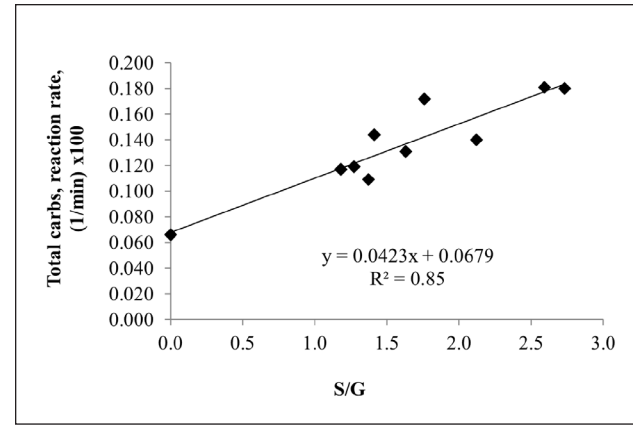
It was determined that the rate of carbohydrate degradation for all three carbohydrate fractions (glucan, xylan and total carbohydrates) was also correlated to the S:G ratio of the lignin. The correlation between S:G and glucan dissolution was quite weak ($R^2 = 0.50$), but indicated a relationship between them. A much better correlation ($R^2 = 0.77$) between xylan dissolution rate and the S:G ratio was found (not shown).

Units	RO	SG	MA	RA	CW	ACA	GLO	EN	URO
β-O-4 total	60	58	58	59	55	58	61	59	62
OMe	169	161	160	160	151	159	175	174	168
Total hydroxide (OH)	161	151	158	149	142	145	161	157	153
Aliphatic OH	132	120	134	126	118	120	136	131	128
Primary OH	74	65	79	72	66	67	80	74	75
Secondary OH	58	55	55	54	52	53	56	57	53
Phenolic OH	29	31	23	22	19	23	21	24	24
Degree of									
Condensation	21	23	22	25	16	23	17	15	20
Syringyl:Guaiacyl lignin ratio	2.13	1.61	1.20	1.37	1.41	1.15	2.73	2.59	1.76

II. Main lignin structures in hardwoods - #/100 C9 units for* Eucalyptus nitens *(EN),* E. globulus *(EG),* E. urograndis *(URO), sweet gum (SG), red maple (MA), red oak (RO), red alder (RA), cottonwood (CW), acacia (ACA), and loblolly pine (P).



6. Carbohydrates degradation ratio as a function of syringyl:guaiacyl lignin ratio.



7. Delignification ratio as a function of carbohydrates degradation.

When the total carbohydrate dissolution rate, which includes the dissolution of all hemicelluloses and cellulose, was evaluated (**Fig. 6**), an even higher correlation was observed ($R^2 = 0.85$).

The correlation of lignin structure (S:G) to carbohydrate dissolution rate appears to be an indirect relationship. The wood cell wall contains not only cellulose, hemicellulose, and lignin but also pectins, extractives, and trace metals. All of these components interact with each other and form a complex matrix. Lignin, in this matrix, is known to cross-link to different polysaccharides, contributing to wood rigidity [35-39].

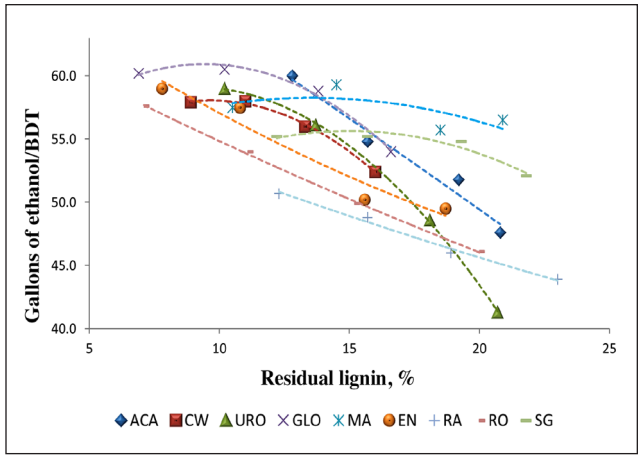
This close interaction among wood cell wall components seems to be responsible for the higher degradation of carbohydrates for species containing high amounts of syringyl lignin units. Because a higher S:G ratio provides greater lignin removal [27], we might assume that high molecular weight carbohydrate polymers become solvated by the cooking liquor at a higher rate and this might be responsible for the higher carbohydrate degradation rate. The hypothesis we propose relies on the fact that lignin and its configuration in the wood matrix acts as a protective coating around cellulose and hemicellulose. Wood species with high syringyl lignin content have superior delignification. The greater rate of lignin removal exposes more of the carbohydrates, allowing for easier and faster white liquor accessibility, and thus, easier and faster reactions for degradation of carbohydrates. This is especially confirmed when looking at the superior correlation of S:G with total carbohydrates (Fig. 6), which include degradation of all hemicelluloses. Hemicelluloses are intermediates for cellulose association through lignin [40-42] which gives interconnection to the secondary wall [43,44]. Hemicelluloses in the matrix have been reported to be associated with condensed type lignin and in a more advanced stage of cell wall growth, to noncondensed lignin moieties also. This association is believed to be an indication of lignin-carbohydrate complex formation in which lignin-to-hemicellulose bonds establish an essential element of secondary cell wall formation [45].

Carbohydrate degradation versus delignification rate

Figure 7 also confirms the relationship between lignin and carbohydrate degradation, where delignification reaction constants for the different wood species [27] are plotted against carbohydrate degradation constants. A straight line was obtained, which indicates higher carbohydrate degradation for species with high lignin removal for a fixed time. It seems that delignification and carbohydrate dissolution rates are closely linked, and this association appears to be responsible for the higher carbohydrate dissolution rates being correlated with the higher delignification rates. The rate of delignification was 13 times higher than the rate for carbohydrate dissolution.

Studies on the association of lignin and carbohydrates have demonstrated that covalent bonds exist between lignin and all major polysaccharides, (arabinoglucu-ronoxylan, galactoglucomannan, glucomannan, pectins, and cellulose), and that cross-linkages also exist among them [36,37,46]. LCC content is known to be responsible for low delignification and hard to remove lignin during the residual stage of cooking [47]. While evaluating LCC linkages, Obst [48] observed that pine and aspen had different LCC contents. Pine LCC content (ester + ether) was of 4.7 per 100 monomeric lignin units, but aspen had only 0.9 per 100 monomeric lignin units. More recently, Balakshin [47] also found variation in LCC content among different wood species. Total LCC content (ether + phenyl glycoside + esters) in pine was determined to be 7.7, and birch was determined to have 10.2 LCCs per 100 monomeric lignin units. Phenyl glycosides, benzyl ethers, and benzyl esters have been suggested as the main types of lignin-carbohydrate bonds in wood [47].

Species morphological aspects, such as fiber length, fiber diameter, cell wall thickness, percent of fines and vessels, and vessels diameter, have been determined and correlated to delignification rate in a previous paper by comparing the extent of reaction and reaction products with wood meal and wood chips [26]. That study concluded that no



8. Gallons of ethanol per moisture-free short ton of initial feedstock versus residual lignin content in the resulting pulp for* Eucalyptus nitens *(EN),* E. globulus *(EG),* E. urograndis *(URO), sweet gum (SG), red maple (MA), red oak (RO), red alder (RA), cottonwood (CW), acacia (ACA), and loblolly pine (P).

morphological influence on delignification rate was detected, and the same argument can be extended to carbohydrates degradation rate.

Influence of chemical characteristics on cellulosic ethanol production

One of the most important aspects when evaluating the conversion of biomass to liquid biofuels is the quantity of fuel that can be obtained from the raw material used. The number of gallons per moisture-free short ton of feedstock varies widely among the kraft pretreated species (**Fig. 8**). As the residual lignin content (lignin left in the substrate after pretreatment) of the samples decrease, higher amounts of ethanol are produced. The increase in ethanol production is mainly the result of improved enzymatic hydrolysis efficiency, even though more carbohydrates are being lost during pretreatment. Literature studies [49,50] have suggested that the lignin content in the substrate negatively impacts the amount of sugar converted to fermentable monomeric sugars. Figure 8 shows production of gallons of ethanol (yield) from 41 to 61 gal/moisture-free short ton of substrate. Figure 8 also shows that, even when differing species had the same residual lignin content, the gallons of ethanol produced were not the same. This effect was more pronounced in samples with higher lignin content. The difference in yield produced for the diverse species shows the importance of the evaluation of different feedstocks when considering industrial production of ethanol. If a pretreatment process is used where the lignin removal is high, the impact of wood species is expected to be small, because the resulting residue will have a low lignin content. In a previous publication [50], a comprehensive study on the difference in enzymatic hydrolysis for species with the same lignin content showed that the amount of enzyme adsorbed on the substrate after pretreatment, the ratio of syringyl to guaiacyl (S:G) lignin, and the amount of phenolic hydroxide of species with the same lignin content are responsible for the variation in enzymatic hydrolysis performance and in the present case, the gallons ethanol per moisture-free short ton of initial feedstock.

CONCLUSIONS

This study compared 10 industrially important hardwood species in terms of delignification performance. 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.

The rate of carbohydrate dissolution followed the rate of wood delignification, with the rate of delignification being 13 times higher than the rates for carbohydrate dissolution. Higher delignification resulted in higher carbohydrate degradation. LCCs content and interactions between carbohydrates and lignin appear to be the drivers to high carbohydrate degradation at high S:G ratios. As lignin is removed, carbohydrates are removed as well, but at a lower rate.

Species chemical characteristics, especially the ones facilitating lignin removal (such as the S:G ratio) were the main ones that correlated well with increased production of gallons of ethanol per moisture-free short ton. **TJ**

ACKNOWLEDGEMENT

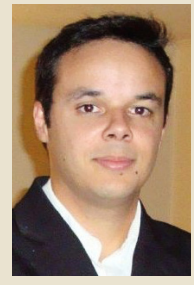
Information from this study was presented at the 2012 TAPPI PEERS Conference and also published as "Impact of lignin and carbohydrate chemical structures on degradation reactions during hardwood kraft pulping processes," *BioResources* 8(1): 158(2013). The current manuscript has added new material around biofuels production.

LITERATURE CITED

1. Gierer, J., *Wood Sci. Technol.* 14(4): 241(1980).
2. Chiang, V.L., Cho, H.J., and Puumala, R.J., *Tappi J.* 70(2): 101(1987).
3. Sarkanen, K.V. and Hergert, H.L. in *Lignins: Occurrence, Formation, Structure and Reaction*, (K.V. Sarkanen and C.H. Ludwig, Eds.), Wiley-Interscience, New York, 1971.
4. Akiyama, T., Goto, H., Nawawi, D.S., et al., *Holzforschung* 59(3): 276(2005).
5. Dimmel, D., MacKay, J., Courchene, C., et al., *J. Wood Chem. Technol.* 22(4): 235(2002).
6. Dimmel, D., MacKay, J., Althen, E., et al., *J. Wood Chem. Technol.* 21(1): 1(2001).
7. Collins, D.J., Pilotti, C.A., and Wallis, A.F.A., *Appita J.* 43(3): 193(1990).
8. Pinto, P.C., Evtuguin, D.V., and Neto, C.P., *Ind. Eng. Chem. Res.* 44(26): 9777(2005).
9. González-Vila, F.J., Almendros, G., del Rio, J.C., et al., *J. Anal. Appl. Pyrolysis* 49(1-2): 295(1999).
10. Bose, S.K., Francis, R.C., Govender, M., et al., *Bioresour. Technol.* 100(4): 1628(2009).

11. Tsutsumi, Y., Kondo, R., Sakai, K., et al., *Holzforschung* 49(5): 423(1995).
12. Chang, H.-M., and Sarkanen, K.V., *Tappi* 56(3): 132(1973).
13. Gomes, F.J.B., Gouvêa, A.F.G., Colodette, J.L., et al., *O Pap.* 69(12): 95(2008).
14. del Río, J.C., Gutiérrez, A., Hernando, M., et al., *J. Anal. Appl. Pyrolysis* 7: 110(2005).
15. Gomide, J.L., Colodette, J.L., Oliveira, R.C., et al., *Revista Árvore* 29(1): 129(2005).
16. Guerra, A., Elissetche, J.P., Norambuena, M., et al., *Ind. Eng. Chem. Res.* 47(22): 8542(2009).
17. Sixta, H. and Rutkowska, E.W., *Lenzinger Ber.* 86: 32(2006).
18. Simão, J.P.F., Egas, A.P.V., Baptista, C.M.S.G., et al., *Ind. Eng. Chem. Res.* 44(9): 2990(2005).
19. Simão, J.P.F., Egas, A.P.V., Baptista, C.M.S.G., et al., *Ind. Eng. Chem. Res.* 44(9): 2997(2005).
20. Gilarranz, M.A., Santos, A., Garcia, J., et al., *Ind. Eng. Chem. Res.* 41(8): 1955(2002).
21. Santos, A., Rodriguez, F., Gilarranz, M.A., et al., *Ind. Eng. Chem. Res.* 36(10): 4114(1997).
22. Giudici, R. and Park, S.W., *Ind. Eng. Chem. Res.* 35(3): 856(1996).
23. Mirams, S. and Nguyen, K.L., in *Fundamentals and Applications in Pulping, Papermaking, and Chemical Preparation: The 1995 Forest Products Symposium*, AIChE Symposium Series No. 311, Vol. 92, American Institute of Chemical Engineers, New York, 1996, pp. 1-9.
24. Johansson, D., "Carbohydrate degradation and dissolution during kraft cooking," licentiate thesis, Karlstad University, Karlstad, Sweden, 2008.
25. Dence, C.W. and Lin, S.V., *Methods of Lignin Chemistry*, Springer-Verlag, Berlin, Germany, 1992.
26. Lee, J.M., Shi, J., Venditti, R.A., et al., *Bioresour. Technol.* 100(24): 6434(2009).
27. Santos, R.B., Capanema, E.A., Balakshin, M.Y., et al., *BioResources* 6(4): 3623(2011).
28. Capanema, E.A., Balakshin, M.Y., Kadla, J.F., et al., *O Pap.* 68(5): 74(2007).
29. Bjorkman, A., *Sven. Papperstidn.* 59: 477(1956).
30. Wilder, H.D. and Daleski, E.J., *Tappi* 48(5): 293(1965).
31. Kleinert, T.N., *Tappi* 49(2): 53(1966).
32. Lai, Y.-Z. and Sarkanen, K.V., *Cellul. Chem. Technol.* 1(5): 517(1967).
33. Santos, R.B., "Influence of lignin structure on chemical bioconversion processes," doctoral dissertation, North Carolina State University, Raleigh, NC, USA, 2012.
34. Santos, R.B., Capanema, E.A., Balakshin, M.Y., et al., *J. Agric. Food Chem.* 60(19): 4923(2012).
35. Liu, F.P. and Rials, T.G., *Langmuir* 14(2): 536(1998).
36. Lawoko, M., Henriksson, G., and Gellerstedt, G., *Holzforschung* 60(2): 156(2006).
37. Lawoko, M., Henriksson, G., and Gellerstedt, G., *Biomacromolecules* 6(6): 3467(2005).
38. Henriksson, G., Lawoko, M., Martin, M.E.E., et al., *Holzforschung* 61(6): 668(2007).
39. Whetten, R., and Sederoff, R., *Plant Cell* 7: 1001(1995).
40. Fry, S.C., *Ann. Rev. Plant Physiol.* 37: 165(1986).
41. Newman, R.H., *Holzforschung* 46(3): 205(1982).

ABOUT THE AUTHORS



Santos

Jameel

Chang

Hart

The topic was chosen because not many studies have looked at so many different hardwood species in such a comprehensive manner.

The most difficult parts of the study were raw material acquisition and comprehensive lignin analysis.

I have personally learned a lot from this research. It was interesting to find how hardwood species can differ from each other in chemical composition and the impact of those differences in bioconversion processes.

This study brings a very comprehensive look at the effect hardwood species have on pulping processes. It can be used from species selection at the forest to process optimization at the mill. It also adds support to the developing biofuel industry.

The next step is already being taken. We are continuing the study by looking at the kinetics of the initial phase of kraft cooking. We are using the same wood species previously used.

Santos is applied technology specialist and Hart is manager, new products, MeadWestvaco Corporation, Richmond, VA, USA. Chang is professor emeritus and Jameel is Ellis Signe Olssen professor, Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, USA. Email Santos at balleirini@gmail.com.

42. Iiyama, K., Lam, T.B.-T., and Stone, B.A., *Plant Physiol.* 104(2): 315(1994).
43. Anterola, A.M. and Lewis, N.G., *Phytochem.* 61(3): 221(2002).
44. Ha, M.-A., MacKinnon, I.M., Sturkova, A., et al., *Phytochem.* 61(1): 7(2002).
45. Ruel, K., Chevalier, V.B., Guillemin, F., et al., *Maderas: Cienc. Tecnol.* 8(2): 107(2006).
46. Li, A., and Khraisheh, M., *Int. J. Chem. React. Eng.* 8(1): A85(2010).
47. Balakshin, M.Y., Capanema, E.A., and Chang, H.-M., *Holzforschung* 61(1): 1(2007).
48. Obst, J., *Tappi* 65(4): 109(1982).
49. Yu, Z., Jameel, H., Chang, H.-M., et al., *Bioresour. Technol.* 102: 9083(2011).
50. Santos, R.B., Lee, J.M., Jameel, H., et al., *Bioresour. Technol.* 110: 232(2012).

PEERS
SEPTEMBER 15-18, 2013
Green Bay, Wisconsin

Pulping
Engineering
Environmental
Recycling
Sustainability

Sustainable Manufacturing: 1st and Goal!

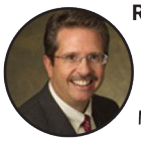
For 2013, the TAPPI PEERS Conference will move north and will continue a tradition of excellent programming designed to help you optimize mill operations with:

- Peer-reviewed Technical Sessions
- Rountable and Panel Discussions
- Networking and Exhibits
- New Technology Showcase
- Hot Topic Breakfasts

Program updates, registration and hotel information are available at:

tappipeers.org

Keynote Speaker



Robert A. Feeser
Senior VP
Food & Beverage
Packaging
MWV

Courses and Workshops

Process Control of Stickies Workshop
September 15, 2013

Fixed Equipment Maintenance Optimization Seminar (FEMOS)
September 15, 2013

TAPPI Biorefinery Course
September 15-17, 2013

Bleach Plant Workshop
September 15, 2013

Kraft Pulp Mill Lime Recovery Kiln Maintenance Workshop
Thursday, September 19, 2013

Co-Located with:

IBBC 2013 International Bioenergy & Bioproducts Conference
September 18-20 • Green Bay, Wisconsin

10TH RESEARCH FORUM ON RECYCLING
SEPTEMBER 15-18, 2013