Impact of Lignin and Carbohydrate Chemical Structures on Degradation Reactions during Hardwood Kraft Pulping Processes

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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 on both lignin and carbohydrate degradation during kraft pulping of multiple hardwood species. The kraft delignification rates of *E. urograndis, E. nitens, E. globulus*, sweet gum, maple, red oak, red alder, cottonwood, and acacia were obtained. Furthermore, the kinetics of glucan, xylan, and total carbohydrate dissolution during the bulk phase of the kraft pulping process for the above species were also investigated. The wide ranges of delignification and carbohydrate degradation rates were correlated to wood chemical characteristics. It appears that the S/G ratio and lignin-carbohydrate-complexes (LCCs) are the main characteristics responsible for the differences in kraft pulping performance among the hardwoods studied.

Keywords: Kraft; Delignification; Carbohydrate degradation; LCC; Syringyl lignin; Guaiacyl lignin; S/G; S/V

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INTRODUCTION

Kraft pulping is currently the dominant chemical process 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 to other processes, especially in terms of fiber strength. Disadvantages are also present, with the loss in pulp yield caused by carbohydrate instability (dissolution, peeling, and degradation during the alkaline reaction) being the major ones. In order to minimize these losses, it is important to have a good and reliable understanding of both the chemical process and the raw material employed in the cook. Furthermore, interactions between process conditions and the utilized raw material can be critical and may require special attention.

During the kraft pulping process, white liquor promotes lignin dissolution and consequent fiber liberation. The kraft pulping process goes through three distinct phases as the wood chips are cooked into pulp. These phases are the initial phase, the bulk phase, and the residual phase. Significant amounts of carbohydrates are lost during the initial phase due to dissolution and in the bulk and residual phases due to degradation. The bulk phase is known to promote 60% to 68% of the total delignification of the wood (Gierer

1980; Chiang *et al.* 1987). Wood containing lignin that can be easily removed can result in less harsh process conditions, which leads to carbohydrate preservation.

When one discusses wood delignification *vs*. 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 (Sarkanen and Hergert 1971; Akiyama *et al.* 2005), 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 both 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 may allow for a reduced alkali charge, lower cooking temperature, and/or decreased retention time. As these conditions result in milder cooking conditions, an increase in pulp yield and fiber quality may be expected (Dimmel *et al.* 2001, 2002).

Considerable variation in kraft pulping performance of different hardwood species has been reported (Collins *et al.* 1990; Pinto *et al.* 2005; Gonzalez-Vila *et al.* 1999; Bose *et al.* 2009). 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 (Tsutsumi *et al.* 1995). Since *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 (Collins *et al.* 1990; Pinto *et al.* 2005; Gonzalez-Vila *et al.* 1999; Bose *et al.* 2009; Chang and Sarkanen 1973; Gomes *et al.* 2008). Even within the same species of *E. globulus*, 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 (Gonzalez-Vila *et al.* 1999; del Rio *et al.* 2005). Similar results were also reported for various clones of *E. grandis* and the hybrid of *E. grandis* × *E. urophylla* (Gomide *et al.* 2005; Guerra *et al.* 2009). 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 may also play a role in delignification reactions (Guerra e*t al.* 2009). A least one study has suggested that the stereochemistry associated with the *β*-O-4 ether linkage may play an important role in delignification reactions as well (Akiyama *et al.* 2005).

As with delignification, three different reaction steps are known to result in the degradation of carbohydrates during kraft pulping. These reaction steps include 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 (Sixta and Rutkowska 2006).

Acetyl groups from xylan and galactoglucommannans are readily hydrolyzed at the beginning of the cook. Carbohydrate yield loss occurs mainly due to extensive degradation of hemicelluloses, which have both a low degree of polymerization and a predominantly amorphous nanostructure. 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 (Simão *et al.* 2005a,b). Cellulose is relatively resistant to kraft pulping liquor (white liquor).

Carbohydrate degradation of softwood has been the focus of a large number of 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 upon the dissolution of the wood components have produced models which 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 upon the understanding of carbohydrate/lignin behavior of a single wood species (Gilarranz *et al.* 2002; Santos *et al.* 1997).

Also most studies 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 (Giudici and Park 1996). In the same study, the authors 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 (Mirams and Nguyen 1996) 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 (2008) found that degradation of xylan and cellulose from softwood is facilitated 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 chemical features (lignin content and structure and carbohydrates content) of *E. urograndis, E. nitens, E. globulus*, sweet gum, maple, red oak, red alder, cottonwood, and acacia.

EXPERIMENTAL

Raw Material

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) (TAPPI 1998-1999), dried, and used for pulping and lignin isolation.

Sawdust Delignification and Carbohydrates Degradation Rate Constant

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 oven-dried (OD) extracted wood meal plus 30 mL of 25% sulfidity white liquor. Excess white

liquor (liquor: wood ratio of 10:1) was used in order to maintain nearly constant reagent concentrations during the kinetic experiments. Therefore, the active alkaline charge was 40% on OD wood. The autoclaves were closed and placed into the M&K 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 M&K digester. This procedure was used to ensure the same heat transfer properties inside the autoclaves and the fluid that is heating them, which is controlled by the M&K digester. After the desired reaction time, the whole apparatus was cooled down 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 (Dence and Lin 1992) were then determined for kinetics calculations.

Carbohydrate Analysis

The samples' carbohydrate composition was determined by acid hydrolysis (Santos *et al.* 2011). A sample weight of 0.1 g was hydrolyzed with 1.5 mL of 72% H_2SO_4 at room temperature with occasional stirring for 2 h. The mixture was then diluted to 3% H_2SO_4 using deionized water, transferred to a vial, sealed, and heated to 120°C for 1.5 h. The resulting suspension was filtered, and the filtrate was analyzed for monomeric sugar units. Fructose 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 (HPAE-PAD) on a Dionex IC-3000 chromatography system. Sugars were separated using a Carbo-Pac PA1 guard and analytical columns 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 NaOH 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

^{13}C-NMR analysis was performed according to the method of Capanema *et al.* (2007). ^{13}C-NMR spectra of the lignin preparations in DMSO-d6 were recorded on a Bruker AVANCE 300 MHz spectrometer at 300 K (27ºC) using a 90º 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.* (2007), where all samples were extracted with 0.3% NaOH for 1 h to remove tannins. The ball-milled wood was extracted with 96% aqueous p-dioxane, in accordance with the method of Bjorkman (1956). 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 20,000 scans were collected.

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). As polymers such as carbohydrates and extractives consume part of the alkaline solution, 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 150ºC for four different time periods (20, 30, 45, and 60 minutes).

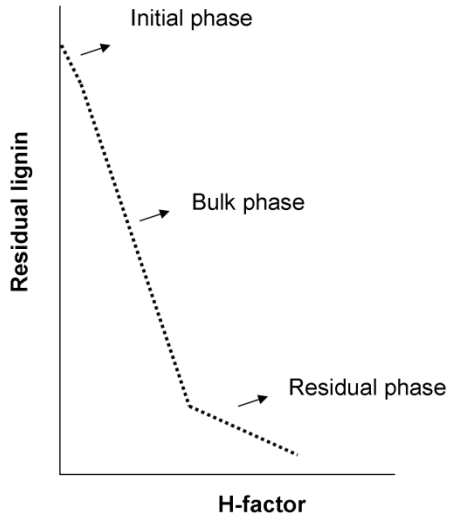

Fig. 1. The three cooking phases

All species studied presented a pseudo-first order reaction for delignification and carbohydrate degradation. Pseudo-first order reaction was found to be in good agreement with previous studies (Sixta and Rutkowska 2006; Wilder and Daleski 1965; Kleinert 1966; Lai and Sarkanen 1967).

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 Equation 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 (Chang and Sarkanen 1973; Santos *et al.* 2011).

Examples of how the rates were obtained are provided in Fig. 2. Rates were calculated using the exponential equation shown in each curve.

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%.

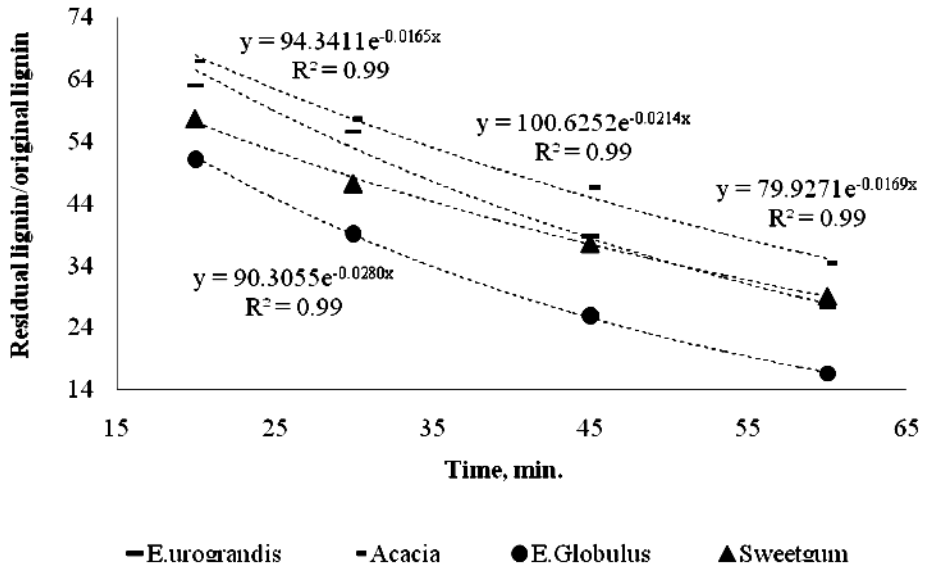

Fig. 2. Rate constants from exponential equations

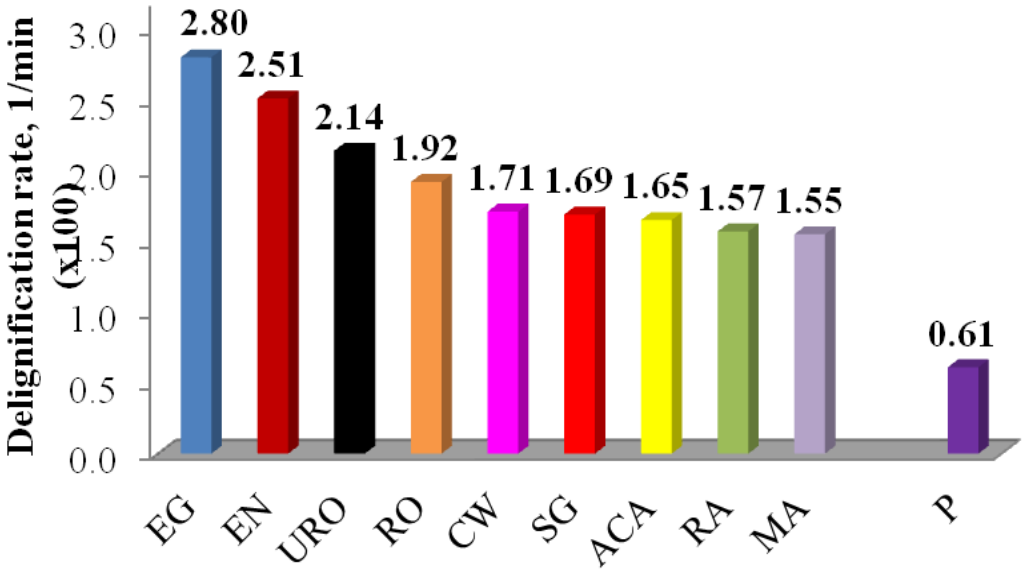

Fig. 3. Delignification rates for *E. nitens* (EN), *E. globulus* (EG), *E. urograndis* (URO), sweet gum (SG), red maple (MA), red oak (RO), red alder (RA), cottonwood (CW), acacia (ACA), and loblolly pine (P)

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 1 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 presented 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 1). In general, hemicelluloses are more easily degraded under alkaline conditions than cellulose due to their low degree of polymerization and lower degree of crystallinity (more amorphous regions) (Santos 2012). The relative standard deviation for the experiments was 2.6%.

Table 1. Glucan and Xylan Degradation Rates

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

* Refer to Fig. 3 for abbreviations definition.

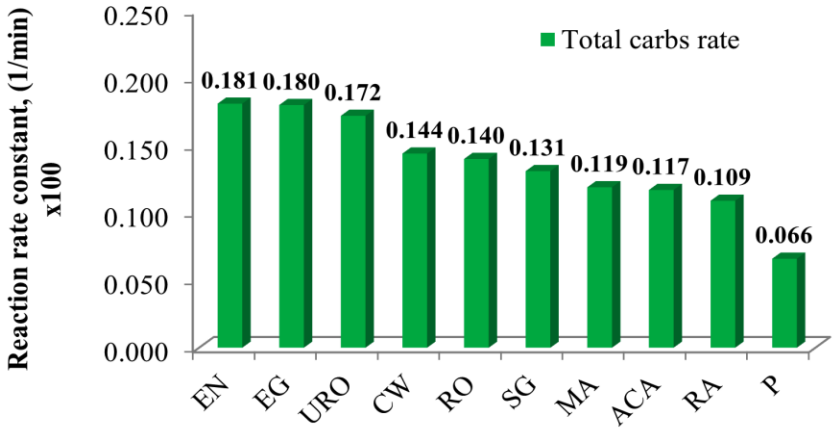

Fig. 4. Total carbohydrates degradation rates. Refer to Fig. 3 for abbreviations definition.

Impact of Lignin Structure on Delignification and Carbohydrates Degradation Kinetics

In order 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 (refer to Santos *et al.* 2012 for complete NMR characterization), and fiber morphologies were correlated with the rate constant values. Other than lignin structure, no other chemical/morphological (Santos *et al.* 2012) feature appears to have an impact on delignification or carbohydrates degradation rates.

Relationship between wood delignification and lignin structure

The main lignin structures quantified on hardwood species are shown in Table 2. 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 (Santos *et al*. 2012). 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 can also 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 employed 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. The main idea is to make the substrate more accessible to enzymes.

Table 2. Main Lignin Structures in Hardwoods - #/100 C9 units

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 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
S/G	2.13	1.61	1.20	1.37	1.41	1.15	2.73	2.59	1.76

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 (not shown), was quite weak (R^2 = 0.50), but indicates a relationship between them. On the other hand,

a much better correlation (R^2 = 0.77) between xylan dissolution rate and the S/G ratio was found (not shown). 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 (Liu and Rials 1998; Lawoko *et al.* 2005, 2006; Henriksson *et al.* 2007; Whetten and Sederoff 1995).

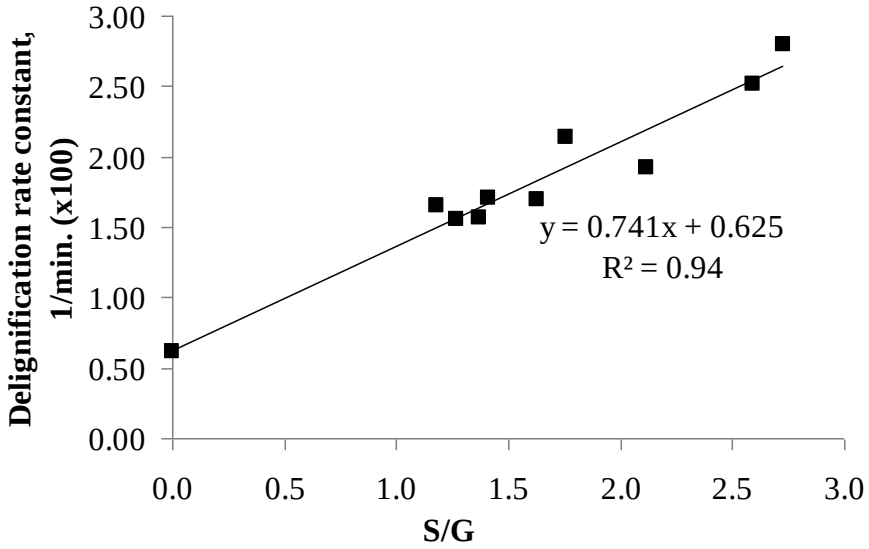

Fig. 5. Delignification ratio as a function of S/G ratio

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. Since higher S/G ratio provides greater lignin removal (Santos *et al.* 2011), it is reasonable to assume that high molecular weight carbohydrate polymers become solvated by the cooking liquor at a higher rate and this may 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/faster white liquor accessibility and thus easier/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 (Fry 1986; Newman 1992; Iiyama *et al.* 1994) which gives interconnection to the secondary wall (Anterola and Lewis 2002; Ha *et al.* 2002). 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 non-condensed 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 (Ruel *et al.* 2006).

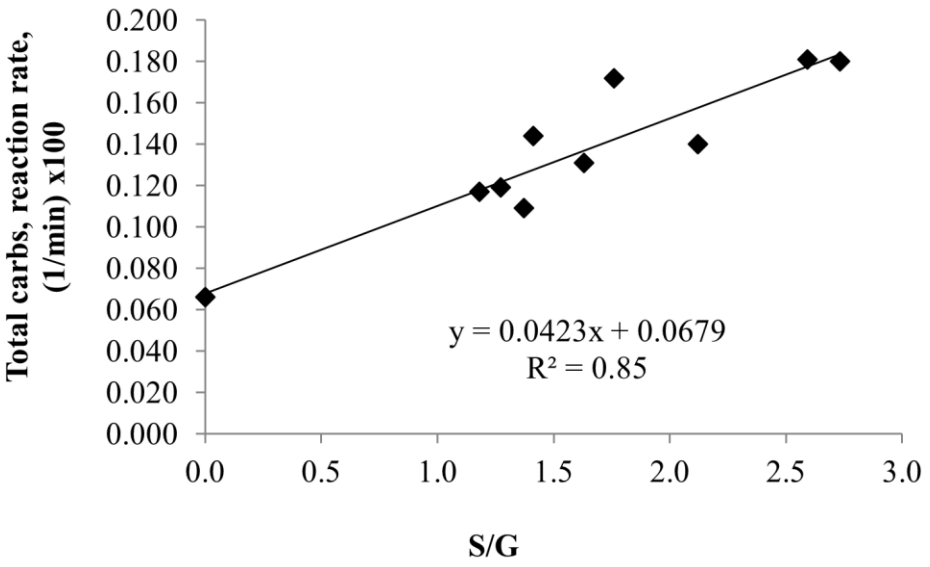

Fig. 6. Carbohydrates degradation ratio as a function of S/G ratio

Carbohydrate degradation versus delignification rate

The relationship between lignin and carbohydrate degradation is also confirmed in Fig. 7 where delignification reaction constants for the different wood species (Santos *et al.* 2011) 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 found to be thirteen times higher than the rate for carbohydrate dissolution.

Studies on the association of lignin and carbohydrates have demonstrated that not only covalent bonds exist between lignin and all major polysaccharides, (arabinoglucuronoxylan, galactoglucomannan, glucomannan, pectins, and cellulose), but that cross-linkages also exist among them (Liu and Rials 1998; Lawoko *et al.* 2005, 2006). LCC content is known to be responsible for low delignification and/or hard to remove lignin during the residual stage of cooking (Balakshin *et al.* 2007). While evaluating LCC linkages, Obst (1982) observed that pine and aspen had different LCC contents. While pine LCC content (ester + ether) was of 4.7 per 100 monomeric lignin units, aspen had only 0.9 per 100 monomeric lignin units. More recently Balakshin (2007) also found variation in LCC content among different wood species. While total LCC content (ether + phenyl glycoside + esters) in pine was determined to be 7.7, 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 (Balakshin *et al.* 2007).

Species morphological aspects such as fiber length, fiber diameter, cell wall thickness, % of fines and vessels, and vessels diameter, have been determined and

correlated to delignification rate in a previous paper (Santos *et al.* 2011). That study concluded that no morphological influence on delignification rate was detected, and the same argument can be extended to carbohydrates degradation rate.

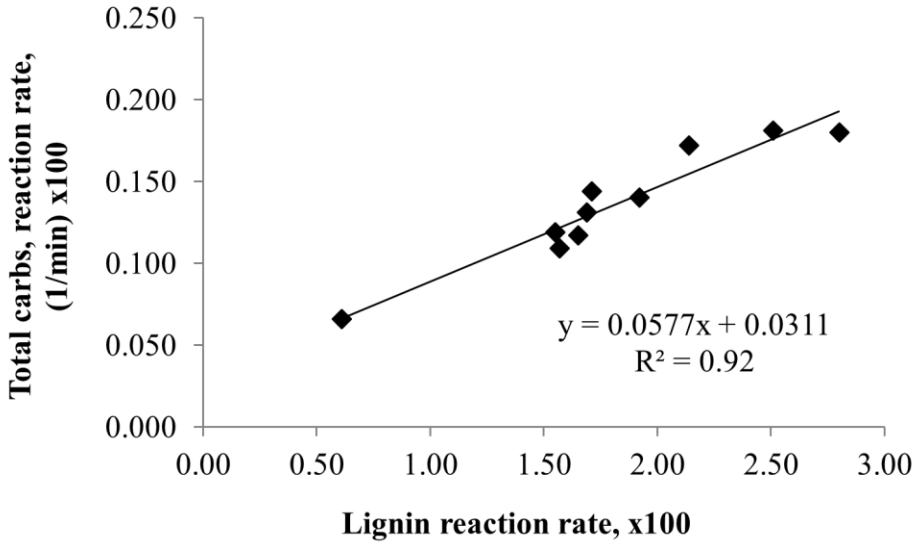

Fig. 7. Delignification ratio as a function of carbohydrates degradation

CONCLUSIONS

1. Ten industrially important hardwood species were compared in terms of delignification performance, and a wide range of delignification rate constants were obtained for the various species. These variations indicate how easy or difficult the delignification process for each species shall be. *Eucalyptus* species were established as the easiest to delignify.
2. 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.

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