Estimation of the S/G ratios of the lignins in three widely used North American hardwoods

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ABSTRACT: Sugar maple (*Acer saccharum*), aspen (*Populus tremuloides*), and white birch (*Betula papyrifera*) are three hardwoods that are widely used by the North American pulp and paper industry. Because of their abundance, these species are also likely to be used by some of the biorefinery processes that are being developed. A significant amount of evidence indicates that the syringyl to guaiacyl (S/G) ratio of the lignin in a hardwood is a governing parameter regarding its ease of delignification. Credible data also show that among poplars the S/G ratio of the lignin significantly influences the ease of saccharification of the carbohydrate polymers to sugar monomers. Although the S/G ratio appears to be a key parameter for hardwoods, values accepted by most practitioners are not available for the three species. In this investigation, those ratios were estimated by an extensive literature review followed by S/G determination by nitrobenzene oxidation (NBO) and methoxyl analyses of organosolv lignin (OSL) from the ethanol/water/sulfuric acid pulping process. The S/G values were approximately 1.4 for sugar maple, and 2.0 for aspen and white birch. Data are also included showing that sugar maple and white birch were equally reactive in kraft pulping. Thus, it is unclear whether or not the S/G ratio is indeed a governing parameter in this delignification process.

Application: The results from this investigation suggest that S/G ratio alone cannot explain the different rates of delignification by kraft liquor typically observed among hardwoods. Mills might benefit from including more sugar maple in their cooking furnish, if possible.

The syringyl to guaiacyl (S/G) ratio is a major or even dominant parameter governing the ease of delignification of hardwoods. S/G data have been reported for kraft pulping under alkaline conditions [1-6] and organosolv pulping (ethanol/water) under acidic conditions [7]. The effect of the S/G ratio also appears to be a major parameter in oxygen delignification [6] and chlorine dioxide (ClO_2) bleaching of hardwood kraft pulps [4,8]. Evtuguin and Pascoal Neto [4] reported especially convincing results showing the greater ease of delignification of syringyl units in kraft pulping. They isolated native lignin from five different hardwood species and their corresponding kraft pulps. The authors examined *Betula pendula*, *Acacia mangium*, and three eucalypti. The S/G ratio of the three eucalypti native lignins fell in a range of ~2.1–5.0, with the corresponding range for the kraft residual lignin (isolated from pulp) being ~1.3–1.7 [4]. The S/G ratio for native versus residual lignin was ~2.4 vs. ~0.7 for the birch (*B. pendula*) and ~1.0 vs. ~0.6 for *A. mangium* [4]. Similar trends in the S/G ratio were later reported by Ventorim et al. [6]. They reported a ratio of ≥1.7 for two eucalypti native lignins, but ≤1.0 for the two corresponding kraft residual lignins [6].

Goyal et al. used autocatalyzed ethanol/water mixtures (with no acid addition) to delignify mixed hardwood chips. The cooking temperature profile was ~30 min to a maximum temperature of 195ºC and up to 150 min at the maximum temperature [7]. The authors observed that after 10 min at 195ºC, the dissolved lignin, when analyzed by proton nuclear magnetic resonance (^{1}H NMR), contained three times more protons from S units than from G units. The authors concluded that S units were preferentially solubilized [7].

Evtuguin and Pascoal Neto [4] examined the effect of S/G ratio on bleaching of the five hardwood kraft pulps. The S/G ratio of the residual lignins of these kraft pulps varied from ~0.6 to 1.7. One of the eucalypti pulp samples had an S/G ~1.7 and consumed 4.4% ClO_2. (as equivalent chlorine gas [Cl_2]) to achieve 90% ISO brightness, while the Acacia pulp sample with S/G ~0.6 consumed 7.4% ClO_2. (as equivalent Cl_2) [4]. The negative linear correlation between S/G ratio and ClO_2 demand had an R^2 value that was >0.98 [4].

In the biorefinery area, a high S/G ratio is reported to be important, at least for poplars. Two investigations involving multiple poplar species (or hybrids) arrived at the conclusion that the ease of saccharification of carbohydrate polymers to sugar monomers increased as the S/G ratio increased [9,10].

The objective of our research was to review the literature and provide new data to the debate on the importance of the S/G ratio. Data from different analytical methods appear to confirm that the S/G ratios for native birch lignins are much

higher than those of maple lignins [11-13]. However, there are also ample data showing that the two genera have nearly equal delignification rates when measured at various stages in the kraft pulping process [5,14]. When a mild acid pretreatment was used ahead of soda-anthraquinone (SAQ) pulping, it appeared that sugar maple and white birch were delignified at approximately the same rate [15].

EXPERIMENTAL

Wood samples

All three hardwood species were harvested from mature trees grown at the Heiberg Memorial Forest, Tully, NY, USA. This forest is owned and managed by the State University of New York, College of Environmental Science and Forestry (SUNY-ESF). Starting with debarked wood chips, wood meals (15 or 30 mesh) were prepared from the three hardwoods. All of the wood meals were soxhlet-extracted using a 2:1 (v/v) mixture of toluene/ethanol before nitrobenzene oxidation (NBO) or organosolv pulping.

A→C (N)→kraft pulping

The A→C (N) acronym denotes a dilute acid pretreatment (A) of the chips followed by carbonate neutralization (C [N]). The A stages were performed with a 4:1 liquor-to-wood (L:W) ratio in a laboratory digester (M/K Systems; Peabody, MA, USA). Acetic acid (2 wt% on an oven-dried chip basis) was added to the water. The temperature of the digester was increased from room temperature to 120°C in 30 min. The digester was then maintained at that temperature for an additional 30 min. Liquor recirculation was continuous during the entire process. After an A stage, the free liquor was drained off through a condenser and an equal volume of sodium carbonate solution (containing 3.0 wt% on initial wood [as Na_2O]) was added. The digester was then heated from ~70°C to 150°C in ~15 min. The C (N) stage (carbonate neutralization) was then continued for 30 min. The C (N) stage effluent was then drained off and replaced with an equal volume of kraft white liquor (sodium hydroxide [NaOH] and sodium sulfide [Na_2S]). An active alkali (NaOH and Na_2S) dose of 16 wt% on initial wood (as Na_2O) and 25% sulfidity were used. The digester was then heated from ~80°C to 165°C in ~20 min and kraft cooking continued for an additional 30 min. The H factor for kraft pulping was 335.

Organosolv treatments

Treatments were performed in stainless steel autoclaves with a volume of ~250 mL. We treated 10 g of 15-mesh wood meal using a 20:1 liquor-to-wood (L:W) ratio. The organosolv liquor consisted of 120 mL of ethanol and 80 mL water/sulfuric acid (H_2SO_4). The H_2SO_4 dosage was 1.65% on wood, which corresponded to a concentration of 8.4×10^{-3} M in the organosolv liquor. The wood meal and organosolv liquor were placed in an autoclave, which was sealed and heated for 2 h in a water bath at 90°C–95°C. The autoclave was vigorously shaken at intervals of ~15 min. After the 90°C–95°C pretreatment, one or two of the autoclaves were placed into the laboratory digester filled with water. The water was heated to 183°C in ~40 min (with circulation) and maintained at that temperature for 60 min. The digester was drained at the end of the treatment and the delignified wood meal (pulp) was separated using a Büchner funnel with low-to-moderate porosity filter paper. The pulp retained on the filter paper was washed with ethanol/water (60:40 v/v). The entire solution phase was concentrated using a roto-evaporator to generate a syrup of low volume (<50 mL). Water was used to dilute, wash, and transfer all of the syrup from the round bottom flask associated with the roto-evaporator into a 1000 mL Erlenmeyer flask. The volume was adjusted to 575 mL with water and H_2SO_4 to give a final H_2SO_4 concentration of 4 wt%. The slurry was refluxed for 30 min. The organosolv lignin (OSL) or acid insoluble lignin was then recovered in a manner similar to the Klason procedure (TAPPI Standard Test Method T-222 om-06 "Acid-insoluble lignin in wood and pulp").

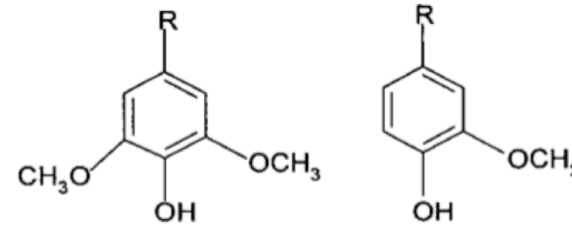
Analyses

NBO was performed in duplicate, as previously described [16]. Klason lignin was determined by TAPPI T-222 om-06. Acid-soluble lignin (ASL) was determined by TAPPI UM-250 "Acid-soluble lignin in wood and pulp." Methoxyl analyses were performed in duplicate by Galbraith Laboratories, Knoxville, TN, USA. A modified Zeisel method (using hydroiodic acid) was used for methoxyl analysis.

RESULTS AND DISCUSSION

Critical review of data on S/G ratios for three hardwoods

Several wet chemistry and spectroscopic methods have been used to estimate the S/G ratio of sugar maple, aspen, and white birch. In this review, we focus on the nitrobenzene oxidation (NBO) method, which quantifies the high molar yields of four monomers (**Fig. 1**). The method has been widely used for more than 50 years, and has a high degree of repeatability and reproducibility [16-18]. A realistic S/G ratio can likely be derived from NBO treatment of extractives-free wood or biomass meal if the combined yields of the V monomer products (vanillin and vanillic acid) of Fig. 1 are ≥13.0 mole %. The total



1. Main products from nitrobenzene oxidation (NBO) of hardwood lignins.

yield of S+G monomer products should also be >40 mole %. This assertion regarding NBO credibility is based on analysis of a wide range of hardwoods using the method in our laboratory [6,16,19,20]. The S/V ratio is calculated from the yields of S (syringaldehyde and syringic acid) and V products. The S/G ratio is then calculated using Eq. (1):

$$S/G = c\ (S/V) \quad (1)$$

The c in Eq. (1) is a correction factor that is normally <1.0. Although a c value as low as 0.33 has been reported [21,22], most investigators report c values equal to 1.0. It is unlikely that the c value would fall outside of the 0.6–1.0 range when a high yield of V products are obtained. Santos et al. [12] analyzed milled wood lignin (MWL) from 10 different hardwood species by NBO and carbon-13 nuclear magnetic resonance (^{13}C NMR). The authors showed that the NBO results correlated quite well with the ^{13}C NMR results when a c value of 0.81 was used in Eq. (1). A value of c = 0.70 can be calculated based on fundamental lignin chemistry assumptions. An uncondensed aromatic ring is defined as one not containing a C-C bond at any ring position other than C-1 (i.e., the "propyl" side chain in most cases) nor connected to another aromatic ring by a diaryl ether linkage. The four main NBO monomer products in Fig. 1 all contain uncondensed aromatic rings, which are assumed to be exclusively derived from uncondensed C_9 lignin units. Alves et al. [23] reported that on average ~90% of the S units in hardwood lignin are uncondensed, whereas ~63% of the G units are uncondensed. If the raw yield of S products is divided by 0.90, while that of the V products is divided by 0.63, a constant of ~0.70 is obtained.

In our previous research, a situation arose where high S/G ratios were obtained for three Moroccan eucalypti wood meals using c = 0.70 [20]. Because the minimum lignin content among the three extractives-free samples was 27.8 wt%, we inferred that the methoxyl contents of the wood meals would be high enough to allow for a fairly accurate estimation of the S/G ratio. The lowest methoxyl content among the three samples was 7.7 wt% on wood [20]. After a methoxyl/aryl ratio is obtained, an S/G ratio can be derived by solving a set of simultaneous linear equations. After correction for methoxyls from non-lignin sources (~0.6% OCH_3 on wood) [20], the three S/G ratios from methoxyl analyses were remarkably close to those derived by NBO using c = 0.70 in Eq. (1). The comparisons (NBO vs. OCH_3 content) for the Moroccan eucalypti were 1.72 vs. 1.72, 1.85 vs. 1.72, and 1.98 vs. 2.06 [20]. If the methoxyls from non-lignin sources were equal to 0.5% instead of 0.6%, then a c value of ~0.80 is obtained for the three Moroccan eucalypti wood meals [20].

Additional support for a c value between 0.6 and 1.0 can be obtained by recent determinations of S/G ratio of Japanese maple (*Acer micranthum*) by time-of-flight secondary ion mass spectrometry (TOF-SIMS) of thin wood wafers and by thioacidolysis [24]. The uncondensed fractions of the S and G units would be expected to be much more reactive in thioacidolysis, as compared to the corresponding condensed fractions, and the assumptions leading to c = 0.70 in NBO should also apply. The previously mentioned research showed that when S/G determinations by TOF-SIMS were compared with those from thioacidolysis, the TOF-SIMS values were only 61% as high as those from thioacidolysis [24]. Assuming that the TOF-SIMS results are accurate, then c would equal 0.61 if the raw yields of syringyl and guaiacyl products from thioacidolysis were to be used as S and V in Eq. (1). When a high yield of total thioacidolysis products is obtained, the method normally affords an uncorrected S/G ratio in the same range as the S/V ratio from NBO [25].

Literature data on S/G of maple species

Data for the S/G ratio of sugar maple lignin is quite sparse (see Appendix). We reported a value of 1.3 (rounded to the nearest 10th). However, the raw S and V product yields from NBO analysis and the c value used in Eq. (1) were not presented or discussed [26]. Other reported results for sugar maple include an uncorrected S/G ~2.0 by thioacidolysis and ~1.5 by pyrolysis (gas chromatography-mass spectroscopy [GC/MS]) [27]. An exceptionally high value of S/G = 3.4 by pyrolysis-GC/MS has also been reported for sugar maple [13]. Data for other maple species suggest that the S/G ratio for sugar maple should be in the lower range among hardwoods. Santos et al. [12] reported an S/G ratio of 1.3 for red maple (*Acer rubrum*) determined by ^{13}C NMR analysis of the MWL and 1.1 determined by NBO analysis of the wood meal (using c = 0.8). The authors determined the methoxyl content of the MWL using a wet chemistry technique. The methoxyl/aryl ratio afforded an S/G ratio of ~1.0 [12,28]. Saito and co-workers [24] noted that Japanese maple had an S/G ratio of 1.1, as determined by TOF-SIMS, and 1.8 as determined by thioacidolysis.

Literature data on S/G of aspen (Populus tremuloides)

More documentation is available on the S/G ratio of aspen lignin than on maple lignin, some of which we have presented and discussed in an earlier publication [19]. The Appendix shows some of the values. A typical S/V ratio for aspen lies near a value of 2.5 (S/G ~2.0). Pepper et al. [29] determined the S/V ratio of aspen wood meal lignin by NBO and alkaline copper oxide (CuO) oxidation. The authors reported S/V values of 2.4 and 2.5 from two NBO runs and 2.4 and 2.4 from two alkaline CuO runs. Other researchers have observed S/V values for aspen from NBO treatment that range from 2.2 [30] to 3.0 [31]. Uncorrected S/G values, reported by investigators using thioacidolysis, also range from 2.2 [32] to 3.0 [31].

Spectroscopic methods for S/G determination of the total lignin in biomass meals are now being developed. Data were recently published that compare the S/G by thioacidolysis to those from two of these methods. The first of the whole cell wall spectroscopic methods is two-dimensional heteronucle-

ar single-quantum correlation nuclear magnetic resonance spectroscopy (2D-HSQC NMR) of extractives-free biomass meals that are converted to gels in perdeuterated dimethyl sulfoxide (DMSO) or a DMSO/pyridine mixture [33,34]. The second method is Raman spectroscopy of pellets made from extractives-free biomass meal [35]. In the recently published manuscript, the S/G ratios for aspen were only presented graphically [35]. However, the authors provided some of the numerical S/G data for aspen for this review [36]. The S/G ratio for aspen was 2.4 by the thioacidolysis and the 2D-HSQC NMR methods [35,36].

Literature data on S/G of birches

Reported S/G ratios for various birch species seem more variable as compared with maple and aspen wood species (Appendix). The reported S/V ratios using the NBO method vary from approximately 2.4 [18] to 3.7 [22,37], and the range using thioacidolysis (without correction) is approximately 2.6 [25] to 3.5 [36,38,39]. However, increases in the S/G ratio above 2.0 do not result in as dramatic an increase in the S content as does increasing the S/G from 1.0 to 2.0. Only ~2% of aromatic rings in birch lignins [2,4] and sugar maple lignin [23,26] are methoxyl-free (i.e., *p*-hydroxyphenyl units [H]). Therefore, S and G units comprise ~98% of the aromatic rings in those lignins. If the S/G ratio were to vary from 1.0 to 2.0 for such lignins, the S content would vary from 49% to 65.4% (a 33% increase). However, varying S/G from 2.0 to 3.0 would cause the syringyl content to increase from 65.4% to 73.5% (only a 12% increase).

Permanganate oxidation can be used to quantify the uncondensed and condensed aromatic rings in lignin samples [2,16]. The yield of aromatic monomers and dimers obtained from permanganate oxidation is the highest when the wood meal or isolated lignin sample have undergone a CuO pretreatment [17,40,41]. The quantification of eight monomers and dimers from the CuO→potassium permanganate ($KMnO_4$) method has been reported in MWL studies of white birch [17] and European birch or *B. verrucosa* [40]. The results are nearly identical for all of the major reaction products and for total molar yields (around 36.4 mole%) [17,40]. No correction factors were applied to the yield data in either investigation. Interestingly, analysis of white birch by NBO afforded S/V ratios of 2.5 for extractives-free wood meal and 2.4 for MWL [18]. The corresponding S/V ratio reported for *B. verrucosa* wood meal was 2.6 [42]. NBO and CuO→$KMnO_4$ analyses suggest that white birch and *B. verrucosa* lignins should have approximately equal S/G ratios.

Bose et al. [16] presented results showing that $KMnO_4$ oxidation of dissolved kraft lignin (without CuO pretreatment) could be used to determine a reliable S/G ratio. Data obtained from Gellerstedt et al. [2], who performed a $KMnO_4$ analysis on dissolved kraft lignin from *B. verruocosa*, were also used to calculate an S/G ratio of 1.9 [16]. If an S/V ratio of 2.6 is assumed and c = 0.8 is used in Eq. (1), then an S/G value of 2.1 is obtained.

The analysis of the whole cell wall by the 2D-HSQC NMR method was previously discussed for aspen. The corresponding results for white birch were S/G = 3.5 by thioacidolysis and S/G = 3.9 by 2D-HSQC NMR [35,36]. From the cumulative data on the S/G ratios of birch lignins, it is estimated that their true values are likely >2.0.

S/G for maple versus birch lignin from the same investigation

One of our primary interests regarding the S/G ratio is its effects on the rate and extent of delignification of hardwood species. In a previous study [26], we determined that sugar maple lignin had a low S/G ratio of ~1.3, which was calculated from an S/V value of 1.8 from NBO analysis and c = 0.70. The previously noted literature review and critical analysis indicated that the S/G ratio for aspen and white birch were ~2.0 or higher. Santos et al. [5,12,28] observed an excellent linear correlation between the S/G ratio and the rate of delignification in the bulk phase of kraft pulping for nine different hardwood species (R^2 = 0.94). The authors examined 10 different hardwood species. However, the investigators did not include the birch data in their regression analysis [5,12,28]. As previously discussed, an S/G of 1.0–1.3 was estimated for red maple by three different methods [5,12,28]. Corresponding S/G values in the range of ~2.5–3.3 were simultaneously estimated by the three methods for *Betula pendula* [5,12,28]. However, the rate constant for bulk phase delignification in kraft cooking was higher for the birch than for the maple, but by <10% [5]. Is the S/G ratio truly a governing parameter in kraft cooking if a temperate hardwood with an S/G ratio twice as high as another temperate hardwood is only slightly more reactive?

The results from the Santos et al. investigations [5,12,28] stood out to us because we have made similar observations in our laboratory studies. Sugar maple and white birch wood chips were treated by the A→C (N)→soda-AQ (SAQ) pulping process [15]. Relatively mild acidolysis (A) was performed at 120ºC on maple and birch chips, but an NaOH dose of 14.0% Na_2O (based on initial chip mass) was used in the SAQ stage for birch, while only 12% Na_2O was used for maple. However, the kappa number for the birch A→C (N)→SAQ pulp was only slightly lower than that for the maple pulp [15]. It was estimated that the delignification rate for the two species were nearly equal in the SAQ stage. Additional published data [14] showed that when sugar maple and white birch chips were cooked with identical kraft liquor and at a 500 H-factor, the resulting unbleached pulps had nearly identical kappa numbers (~36.3).

We reviewed the literature for reports where the S/G ratios were estimated for maple and birch lignins in the same investigation. Obst et al. [11] obtained S/V of 2.4 for red maple and 3.6 for white birch by NBO. Those authors used c = 0.33 and derived an S/G ratio of 0.8 for red maple and 1.2 for white birch. Belleville et al. [13] recently reported S/G values for sugar maple and birch to be 3.4 and 4.5, respectively, as measured by the by pyrolysis-GC/MS method.

As noted previously, our group has significant experience in obtaining high NBO yields for a wide range of hardwoods [6,16,19,20]. A decision was made to use NBO to determine the S/V ratio of sugar maple, aspen, and white birch. The aim was to confirm that aspen and birch did indeed have a significantly higher S/V ratio than the 1.8 determined for sugar maple.

S/V determination using the NBO method

The S and V products were determined in duplicate for the three species. Table I presents the results. The starting material was extractives-free wood meal in all cases. **Table I** gives their total lignin contents. The S1+S2 and V1+V2 (Fig. 1) product yields were very repeatable. On a percentage basis, the largest difference between any duplicate samples was 27.2 % vs. 28.3 % S products observed for sugar maple (4% difference). The S/V ratios were 1.8, 2.4, and 2.6 for the maple, aspen, and birch, respectively (Table I). These values would correspond to an S/G of 1.4, 1.9, and 2.1 if c = 0.8 were to be used in Eq. (1). The values for aspen and birch were consistent with the literature data discussed previously. Also, the present S/V ratios for aspen and birch were based on total NBO product yields >49 mole % (Table I). Based on the accumulated literature and the data in Table I, there is little doubt that aspen and birch lignins have S/G ratios in the range of 2.0 or higher. However, we found less published data for sugar maple, as noted in the literature review. Also, the S/V value of 1.8 in Table I was based on a total NBO product yield of only 43.3%. We deemed it necessary to estimate the S/G ratio of sugar maple by another method, which was methoxyl analysis of OSL from ethanol/H_2O/H_2SO_4 pulping.

Production and analysis of organosolv lignins from ethanol/H_2O/H_2SO_4 pulping

Our research was initiated based on the results of Pan et al. [43] for the pulping process applied to chips from a hybrid poplar. Those authors reported methoxyl contents for 14 lignin samples recovered at >50% yield based on the mass of lignin in the starting chips. The liquor to wood ratio was 7:1 and the ethanol volume fraction varied from 50% to 75% for the 14 runs. The H_2SO_4 dose was either 0.83, 1.00, 1.25, 1.50, or 1.67 wt% on chips, and the cooking temperature varied from 165ºC to 205ºC [43]. When an H_2SO_4 dose of 0.83% on chips (at 180ºC) was used to recover 53% of the starting lignin from the pulping black liquor, the lignin sample had a methoxyl/aryl ratio of 1.64. The use of 1.00% H_2SO_4 on chips at 180ºC to recover 73% of the lignin resulted in a sample with a methoxyl/aryl ratio of 1.60 [43]. The remaining 12 runs were conducted with ≥1.25% H_2SO_4. Those samples had an average methoxyl/aryl ratio of 1.77 [43]. It appeared that acid-catalyzed ethylation was occurring during the pulping runs, which would have produced some ethoxyl groups. Pan et al. quantified their methoxyl content using ^{1}H NMR [43]. It is possible that the methoxyl protons and some of the potential ethoxyl protons would overlap at a shift of ~4 ppm. The

Sample	S Products[2] Mole %	V Products[2] Mole %	S/V Ratio
Sugar maple[1]	27.8	15.5	1.8
Aspen	34.7	14.6	2.4
White birch	36.9	14.3	2.6

[1] Total lignin content (Klason + acid-soluble lignin) of 25.0 wt% for maple, 20.4 wt% for aspen, and 22.3 wt% for birch.
[2] Mole % based on aromatic rings in native lignin.

I. Determination of S/V ratios of extractives-free wood meals by NBO.

^{1}H NMR spectrum for ethoxybenzene is available on the Sigma-Aldrich website [44].

How realistic are methoxyl/aryl ratios in the range of 1.60–1.77 for a poplar lignin and how would these values be converted to S/G ratios? That discussion will be initiated with a key assumption in deriving the previous methoxyl/aryl ratios. The molecular weight of the average aromatic unit in aspen lignin (typically a phenylpropane or C_9 unit) was previously estimated at 210 daltons [19]. A similar value was estimated for sugar maple lignin [23,26] and actually determined for white birch MWL [18]. We assumed an average molecular weight of 210 for the hybrid poplar lignin in determining the previous methoxyl/aryl ratios. Actually, a C_9 molecular weight of 210 was assumed for all the lignins involved in this investigation. As previously stated, only ~2% of aromatic rings in birch lignins [2,4] and sugar maple lignin [23,26] are methoxyl-free. Methoxyl-free units in aspen and other poplar lignins constitute ~5% of the aromatic units because of the presence of ester-linked and ether-linked *p*-hydroxybenzoic acid (*p*-HBA) units [45-48]. The hybrid poplar lignin was assumed to contain ~5% methoxyl-free aromatic units.

If S and G units constitute 95% of the aromatic units in a lignin, then the G content can be determined by Eqs. (2) or (3):

$$1.0G + 2.0(0.95\text{-}G) = m \quad (2)$$

$$G = 1.90 - m \quad (3)$$

Equation (3) is a simplification of Eq. (2). The methoxyl/aryl ratio is m in Eqs. (2) and (3). Also, (0.95-G) would become (0.98-G) in Eq. (2) for maple and birch lignins where S and G units constitute ~98% of the lignin. Equation (3) would then become G = 1.96 – m.

The two lower m values for the hybrid poplar lignin were 1.60 and 1.64. If m = 1.62 is inserted in Eq. (3), a G fraction of 0.28 is obtained. That would result in an S/G of 2.4, i.e., (0.95–0.28)/0.28. This value would be realistic for a poplar lignin. On the other hand, if m = 1.77 were to be inserted in Eq. (3), then an S/G ratio of 6.3 would be obtained. Such a value would be well outside of the expected range.

If the ethanol/H_2O/H_2SO_4 pulping approach were to be

Sample	Lignin Fraction[1], %	Methoxyl Content[2], %	Methoxyl/ Aryl, m	S/G Ratio[3]
Maple (Run 1)	~76	22.4	1.52	1.23
Maple (Run 2)	~76	22.6	1.54	1.33
Aspen	~78	23.3	1.58	1.97
Aspen (duplicate)	~78	23.0	1.56	1.79

[1] Percent lignin recovered and analyzed; based on mass of lignin in starting wood meal.
[2] Percent OCH_3 based on lignin.
[3] G fraction = 1.96 – m for maple and 1.90 – m for aspen (see text and Eqs. [2] and [3]).

II. Estimation of syringyl to guaiacyl (S/G) ratio by methoxyl analysis of lignin from ethanol/H_2O/H_2SO_4 pulping.

Sample	A Stage	Screened	Rejects, %[1]	Kappa
	End pH	Yield, %[1]		Number[2]
Sugar maple	3.7 (3.6)[3]	52.5 (52.8)	0.4 (0.5)	29.8 (30.5)
White birch	3.5 (3.5)	50.1 (50.4)	0.3 (0.4)	28.8 (28.3)

[1] Based on initial chip mass.
[2] Kappa number of screened pulp.
[3] Duplicate results in parentheses.

III. Comparison of sugar maple and white birch in A→C (N)→kraft pulping.

used to estimate the S/G ratio of lignin, then the H_2SO_4 concentration would have to be kept in the lower range. Even then, the approach might overestimate the methoxyl/aryl ratio and ultimately the S/G ratio. However, this was considered a drawback that could be tolerated if a moderately low S/G ratio were to be obtained for sugar maple.

The research was initiated with a trial using 15 mesh extractives-free wood meal from sugar maple. The aim was to see if ~70 % of the starting lignin could be recovered by the crucibles used for filtration of the acid insoluble lignin in the Klason method. In one of their earlier runs, Pan et al. were able to recover ~90% of the starting lignin by filtering their OSL (or acid insoluble lignin) through Whatman no. 1 filter paper [43]. The 0.83% H_2SO_4 dose they used corresponded to a solution phase H_2SO_4 concentration of 1.2×10^{-2} M. As stated in the Experimental section, a concentration of 8.4×10^{-3} M was used in the present investigation. In the initial trial using sugar maple (one run only), an OSL (or acid insoluble lignin) yield in the range of 75%–77% was obtained. The extent of delignification was estimated at ~90% based on the pulp yield and kappa number. The lignin sample was analyzed for its methoxyl content and m = 1.52 was obtained (**Table II**). That value would correspond to a G content of 0.44 and an S content of 0.54 (S/G = 1.23). This S/G value is close to the 1.4 value obtained from NBO (i.e., 1.8 × 0.8). Another OSL was prepared from sugar maple at a later date. The extent of delignification of ~90 % and the 75%–77% OSL recovery were reproduced. On this occasion, m = 1.54 was obtained for the OSL (S/G = 1.33).

We decided to perform ethanol/H_2O/H_2SO_4 pulping of aspen wood meal in duplicate. This was to see if we could obtain results similar to those of Pan et al. [43] for a poplar. The extent of delignification was estimated at ~95% based on the pulp yield and kappa number. The average lignin recovery yield was ~78%. The two lignin samples had m values of 1.58 and 1.56, respectively. The G fractions were 0.32 and 0.34 for the two m values. The corresponding S contents were 0.63 and 0.61. These S and G values afforded S/G ratios of 1.97 and 1.79 (**Table II**). These S/G ratios fall in the expected range for aspen lignin. Therefore, the S/G estimated for sugar maple and aspen by NBO were ~1.4 and ~1.9 (c = 0.80), with the corresponding values from methoxyl analyses of OSL being ~1.3 and ~1.9. It appears that the sugar maple sample used in this investigation did indeed have a low S/G ratio.

A→C (N)→kraft pulping of sugar maple and white birch chips

The experimental data, supported by those in the literature, appeared convincing that the lignin in the birch chip sample in Table I had a significantly higher S/G ratio than the lignin in the sugar maple sample (~2.1 versus ~1.4). The birch and maple chip samples from Table I were used for A→C (N)→kraft pulping. The sugar maple chip sample used in this investigation was different from the one used in the

previous investigation [15] that involved the A→C (N)→SAQ pulping process. However, the white birch samples were the same in both investigations. The A stage used in the present investigation was very mild (30 min at 120ºC with end pH ≥3.5). Such an A stage should cleave a significant fraction of the lignin-carbohydrate complexes [49], but should not cleave much of the lignin's β-O-4 bonds [50]. When the A→C (N)→kraft pulping process was applied to the two chip samples, an end pH of 12.9–13.1 was obtained for all of the kraft black liquors. The H factor in kraft pulping stage was 335. **Table III** shows the results in duplicate for the cooked pulps. An average kappa number of 30.2 was obtained for the maple pulps. A slightly lower value of 28.6 was obtained for the birch samples. Once again, the white birch chip sample was not much more reactive than the sugar maple sample. These results raise doubt as to whether the S/G ratio is indeed a governing parameter in kraft pulping of hardwoods.

CONCLUSIONS

Sugar maple, aspen, and white birch are North American hardwoods that are widely used in the pulp and paper industry. They are also likely to be involved in some large-scale biorefinery processes that are being developed. The S/G ratio of the lignin they contain is known to influence their ease of processing in pulp and paper manufacture. This is also reported to be the case for some biorefinery applications. In this investigation, the S/G ratios of the three lignins were estimated by NBO and by methoxyl analyses of OSLs from two of them. The overall data suggest that the S/G ratio of sugar maple lignin is in the range of ~1.4; a range of ~2.0 was obtained for white birch and aspen lignins. Despite its significantly higher S/G ratio, the birch chip sample was only slightly more reactive than the maple chip sample during kraft cooking. **TJ**

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ABOUT THE AUTHORS

We began this study because we were looking for an explanation as to why sugar maple was so easily delignified by kraft liquor (compared to other hardwoods). The research supports prior results showing kraft cooking to be among the most effective pulping methods for the solubilization of guaiacyl (G) units. G units hinder kraft cooking to a lesser degree compared to other methods.

One of the most difficult aspects of this research was making sure that S/G ratio was not determined on only a small fraction of the lignin. We chose analytical methods that quantified a minimum of 43% of the total lignin. Methoxyl analyses were performed on >75% of the total lignin.

One of the most interesting findings from this study was confirmation that sugar maple lignin is quite reactive under kraft cooking conditions. Consequently, mills might benefit from including more sugar maple in their cooking furnish, if possible.

The next step is to compare maple and birch in other cooking processes

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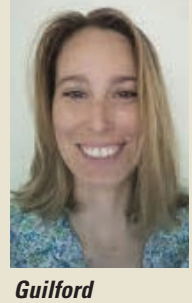
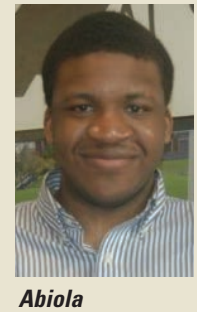
Nicholson


Guilford


Abiola


Bose


Francis

APPENDIX

Compilation of literature data on syringyl to guaiacyl (S/G) ratios for maples, aspen, and birches.

Species	S/G	Method	Reference
Acer micranthum	1.8	Thioacidolysis without CF	24
A. micranthum	1.1	TOF-SIMS	24
A. rubrum	1.3	^{13}C NMR of MWL	12, 28
A. rubrum	1.1	NBO with CF	12, 28
A. rubrum	~1.0	Methoxyl content of MWL	28
A. rubrum	2.4	NBO without CF	11
A. saccharum	1.8	NBO without CF	26
A. saccharum	~2.0	Thioacidolysis without CF	27
A. saccharum	~1.5	Pyrolysis-GC/MS	27
A. saccharum	3.4	Pyrolysis-GC/MS	13
Betula alleghaniensis	4.5	Pyrolysis-GC/MS	13
B. papyrifera	2.5	NBO without CF	18
B. papyrifera	3.6	NBO without CF	11
B. papyrifera	3.5	Thioacidolysis without CF	35, 36
B. papyrifera	3.9	2D-HSQC NMR[1]	35, 36
B. pendula	~2.4	^{13}C NMR of MWL	4
B. pendula	3.2	^{13}C NMR of MWL	12, 28
B. pendula	2.5	NBO with CF	12, 28
B. pendula	~3.3	Methoxyl content of MWL	28
B. verrucosa	2.6	NBO without CF	42
B. verrucosa	3.7	NBO without CF	22, 37
B. verrucosa	2.6	Thioacidolysis without CF	25
B. verrucosa	3.5	Thioacidolysis without CF	38
B. verrucosa	3.4	Thioacidolysis without CF	39
Populus tremuloides	2.2	NBO without CF	30
P. tremuloides	2.5	NBO without CF	29
P. tremuloides	~3.0	NBO without CF	31
P. tremuloides	2.4	Alkaline copper oxide without CF	29
P. tremuloides	~3.0	Thioacidolysis without CF	31
P. tremuloides	2.2	Thioacidolysis without CF	32
P. tremuloides	2.4	Thioacidolysis without CF	35, 36
P. tremuloides	2.4	2D-HSQC NMR[1]	35, 36

CF = correction factor; TOF-SIMS = time-of-flight secondary ion mass spectrometry; ^{13}C NMR = carbon-13 nuclear magnetic resonance; MWL = milled wood lignin; NBO = nitrobenzene oxidation; GC/MS = gas chromatography-mass spectroscopy; 2D-HSQC NMR = two-dimensional heteronuclear single-quantum correlation nuclear magnetic resonance spectroscopy.

[1] Performed on a gel made from extractives-free wood meal.