Bioresource Technology 100 (2009) 1628–1633

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Lignin content versus syringyl to guaiacyl ratio amongst poplars

Samar K. Bose [a], Raymond C. Francis [a,*], Mark Govender [b], Tamara Bush [b], Andrew Spark [b]

[a] Faculty of Paper and Bioprocess Engineering (PBE) and the Empire State Paper Research Institute (ESPRI), SUNY College of Environmental Science and Forestry (ESF), 1 Forestry Drive, Syracuse, NY 13210, USA

[b] Council for Science and Industrial Research (CSIR) and University of KwaZulu-Natal, Forestry and Forest Products Research Centre, P.O. Box 17001, Congella 4013, Durban, South Africa

ARTICLE INFO

Article history:
Received 3 March 2008
Received in revised form 28 August 2008
Accepted 28 August 2008
Available online 26 October 2008

Keywords:
S:G ratio
Poplars
Permanganate oxidation
Nitrobenzene oxidation
Lignin content

ABSTRACT

Two oxidation techniques that afford high yields of monomers and dimers were used to more accurately estimate the syringyl to guaiacyl (S:G) ratio of hardwood lignins. Permanganate oxidation of the woodmeal after a CuO pre-hydrolysis step gave poor results and this was attributed to preferential oxidation and degradation of syringyl nuclei by CuO. However, this procedure did provide a good estimate of the percentages of both S and G phenylpropane (C_9) units that were uncondensed. When the total S and G products from nitrobenzene oxidation (NBO) of the uncondensed fractions were corrected, credible S:G ratios were obtained. These ratios were in good agreement with results from $KMnO_4$ oxidation of dissolved kraft lignin without CuO pre-hydrolysis. The corrected NBO method was used to determine the S:G ratio of 13 poplars, and the values ranged from 1.01 to 1.68. Unlike results from other investigations, an excellent linear correlation ($R^2 = 0.846$) was obtained for a decreasing lignin content (28% to 16.5%) with an increase in the S:G ratio.

1. Introduction

It has long been known that the distribution of cellulose, hemicellulose, total lignin, and lignin substructures is quite variable amongst eucalypt and poplar hybrids. Lignin is the natural glue for cellulosic fibers and is produced by enzyme-mediated radical coupling of the three monolignols in Fig. 1. When incorporated into the lignin polymer the first monolignol (two methoxyl groups) is called a syringyl (S) unit, the second a guaiacyl (G) unit and the third a *p*-hydroxyphenylpropane (H) unit. The use of eucalypt wood for the production of paper and paperboard is increasing at a significant rate and a similar trend is likely to develop for poplars in the more temperate regions. Almost all tree breeding operations in the global pulp and paper industry are trying to select hardwoods with high S:G ratios. This is particularly true for eucalypts and poplars in which this ratio is known to be quite variable. Approximately two-thirds of all virgin wood pulp (recycled fibers excluded) is produced by the kraft process that uses NaOH and Na_2S to extract $\geqslant$90% of the lignin. The rate of this process is believed to be enhanced by a high S:G ratio (Fergus and Goring, 1969; Chang and Sarkanen, 1973; Kondo et al., 1987; Tsutsumi et al., 1995).

On another front, eucalypt and poplar hybrids are two of the primary lignocellulosic feedstock being investigated for the production of ethanol (Ballesteros et al., 2003). Hybrids with low lignin contents would be preferred for many reasons. Principal amongst them would be the higher carbohydrate content of a low lignin feedstock. One question that needs to be resolved is whether or not there is a correlation between lignin content and S:G ratio for eucalypts or poplars when grown on the same site? There are some convincing results showing a decrease in lignin content with increasing S:G ratio for both eucalypts (Yamada et al., 2006) and poplars (Li et al., 2003). However, there are also convincing results showing no correlation between the two variables. No correlation was observed between lignin content and S:G for five *E. globulus* wood samples (10 years old) grown on the same site (Wallis et al., 1996). Also there was no correlation between S:G and total carbohydrate content for seven *E. nitens* (7 years old) grown on another site (Wallis et al., 1996). When six transgenic poplars were grown in the field or greenhouse for 2 years, wood samples with lignin content varying from 18.3% to 19.6% (field) and 17.7% to 21.1% (greenhouse) were obtained (Lapierre et al., 1999). The S:G ratio varied from 0.48 to 1.94 and there was no correlation with lignin content of wood samples from either the field or the greenhouse. Furthermore, kraft pulps were produced from the six poplars under three different conditions and there were no significant differences in pulp yield under all three conditions (Lapierre et al., 1999). Kraft pulp yield is highly correlated with cellulose content for both poplars (Goyal et al., 1999; Francis et al., 2006) and eucalypts (Wright and Wallis, 1998). Therefore, the results by Lapierre et al. would

* Corresponding author. Tel.: +1 315 470 6525; fax: +1 315 470 6945.
E-mail address: francis@syr.edu (R.C. Francis).

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doi:10.1016/j.biortech.2008.08.046

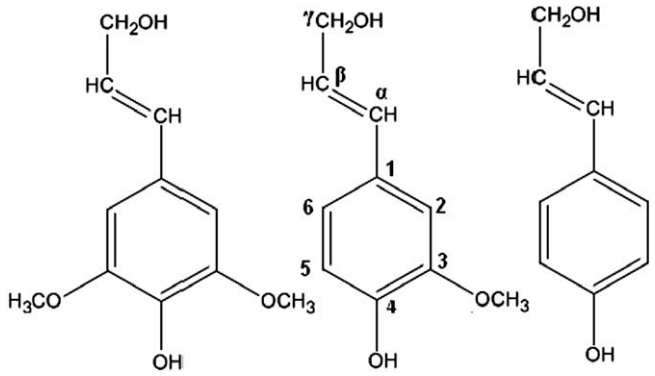

Fig. 1. Monomeric precursors of lignin.

suggest that both lignin and cellulose contents are unaffected by S:G ratio.

This research program was initiated in 2003 and with the primary focus of investigating the effect of S:G ratio on the efficacy of kraft and soda/anthraquinone (SAQ) pulping. At that time it was still unclear whether or not the S:G ratio was a significant variable when kraft pulping was used to produce fibers with kappa number 15–20. The kappa number is the most widely used lignin estimation technique for kraft and other chemical pulps (wt.% lignin $\approx 0.15 \times$ kappa number). Present kraft pulping and bleaching technology requires a kappa number of 15–20 for the unbleached pulp. Bleaching is used to remove the remaining 3–5% lignin from the fibers and transform the pulp color from brown to white. In the investigation by Fergus and Goring (1969) the lowest lignin content after kraft pulping was 6.5% (kappa number approximately 40). Chang and Sarkanen (1973) used only two hardwoods with one being typical of a very low S:G and the other typical of a very high S:G ratio. The syringyl model compounds used by Kondo et al. (1987) and Tsutsumi et al. (1995) were of the most reactive variety. None of them contained a phenylpropane or C_9 unit that was linked to another C_9 by a C–C bond. The evidence is convincing enough that reactive S units are extracted from the cell wall at a higher rate than G units during the rapid or bulk phase of kraft pulping. However, during kraft pulping the transition from the bulk phase to the much slower residual phase occurs at a lignin content of 3–5% on pulp fibers (kappa number of approximately 20–33). There is still no convincing evidence that the initial S:G ratio of the native lignin has any significant effect on delignification rate in the residual phase.

In probably the most detailed of the prior investigations, Collins et al. (1990) determined several wood properties for ten different hardwoods and correlated these properties with the alkali requirement for kraft delignification to kappa number approximately 20. Irrespective of lignin content and wood density the four species with the highest S:G ratios consumed less alkali than the six species with lower S:G ratios. However, amongst the group of four that were all treated with the same alkali dose the species with the lowest S:G (1.20) produced a pulp with kappa number 17.4 while the species with the highest S:G (1.58) afforded a pulp with kappa number 20.1. It was our opinion that the effect of the S:G ratio on kraft pulping was a more complex issue than previously thought and that a much wider range of S:G ratio and more practical kraft pulping conditions were required before definitive conclusions could be drawn. This position was augmented by data from Gomide et al. (2005) obtained during the course of the present research program. Gomide et al. characterized 10 eucalypts and optimized kraft pulping of their chips to attain kappa number 18.0 ± 0.3. The alkali was varied until the target kappa number was attained. Four of the eucalypts required an effective alkali of 15.5–16.0% Na_2O on chips. The four eucalypts had lignin content and S:G ratios of 30.6%, 2.3; 28.2%, 2.1; 29.2%, 2.2 and 27.8%, 2.8, respectively. The S:G ratio appeared to be a non-factor in the range of 2.1–2.8. Furthermore, the sample with lignin content of 27.8% and S:G of 2.8 required 15.8% Na_2O while another eucalyptus with 27.5% lignin and S:G of 2.5 required only 13.7% Na_2O. There was no apparent correlation between ease of kraft delignification and S:G ratio in the range of 2.1–2.8. Nitrobenzene oxidation (NBO) was used to determine S:G ratio and the lowest yield of total oxidation products was greater than 45 phenolic monomers per 100 C_9 units (Gomide et al., 2005).

A major reason for the non-resolution of the controversies associated with the S:G ratio is the absence of a simple and accurate method for S:G determination. Without such a method no research group has been prepared to commit to an investigation involving detailed statistics and enough hardwood logs to cover all of the major variables. Data from NBO will be used to demonstrate some of the discrepancies on S:G ratios in the literature. It has long been known that the NBO yield of guaiacyl products is low and variable (Sarkanen and Hergert, 1971). In a recent investigation, *E. globulus* lignin (dioxane extracted) was analyzed by NBO and approximately 2% of H units, 82–86% S units and 12–16% G units were obtained (Evtuguin et al., 2001). The S:G ratio was >5.0. However, methoxyl analysis by the authors showed only 1.64 OCH_3/C_9 unit. That methoxyl content would correspond to a composition of 2:66:32 (H:S:G) or a S:G ratio of 2.06. On the other hand, Collins et al. (1990) obtained S:G ratios that corresponded to the methoxyl content. However, their syringylaldehyde yields were generally low. The highest yield for ten hardwoods was 22% of the total C_9 units. Syringylaldehyde yields greater than 30% are not uncommon (Gomide et al., 2005; Chen, 1992). Similar to analysis by NBO, S:G ratios >3.5 have also been reported for analysis by pyrolysis/GC–MS (Del Rio et al., 2005) and thioacidolysis (Kuroda et al., 2002). In neither of these two cases was the S:G ratio compared to methoxyl analysis. It should be noted however, that other groups have reported more reasonable values when using these two methods. Actually Rodrigues et al. (1999) obtained a S:G ratio of approximately 2.0 for *E. globulus* using analytical pyrolysis.

The overall objective of this research was to refine the well established nitrobenzene oxidation and permanganate oxidation methods until they gave approximately equal results for the S:G ratio of hardwoods. When this was achieved then S:G ratio would be correlated with lignin content for poplars and the effect of S:G on kraft and SAQ pulping investigated. We are now reporting on refinements to the lignin oxidation methods and the correlation between S:G ratio and lignin content. The effect of S:G ratio on alkaline pulping will be reported separately.

2. Experimental

2.1. Raw materials

Ten experimental poplars were provided by US Forest Service Northern Research Station, Rhinelander, WI. Nine of the poplars were harvested from their Arlington, WI plantation after 9.5 years of growth. Three of these poplars plus another from outside the group were also harvested after 8.5 years of growth. A designation number will be provided for each clone and its parentage is provided in the literature (Riemenschneider et al., 2001). Four commercial poplars were provided by Boise Cascade, LLC from their Wallula, WA plantation. A designation number will be given for each poplar but the parentage was not disclosed by the company. Sugar maple (*Acer saccharum*), white birch (*Betula papyrifera*) and an eastern cottonwood (*Populus deltoids Bartr.*) were obtained from