Partially Hydrolyzing Southern Hardwoods: Possibilities for Biofuels and Wood Composite Manufacturing

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Abstract

Conversion of lignocellulosic materials, including wood, to fuel is currently cost prohibitive due to the expenses involved and the lack of value addition, even though small-diameter hardwoods are readily available. Alternative processes therefore need to be investigated. Partially hydrolyzing wood may offer an opportunity to add value to the conversion process by producing a modified woody by-product that can be used as a wood composite raw material. Experiments were conducted on the effects of a partial hydrolysis on the mass loss, specific modulus, and surface free energy of modified southern hardwoods, and this article reports the changes in holocellulose content of water-saturated yellow-poplar (*Liriodendron tulipifera* L.), sweetgum (*Liquidambar styraciflua* L.), and red oak (*Quercus* spp.) heated at 150°C for 30 minutes in three solutions: 1 percent sulfuric acid, deionized water, and 1 percent sodium hydroxide. The treated woods were compared with untreated controls. The previously tested wood samples were ground to a size 20 mesh, and holocellulose content was analyzed gravimetrically. Properties of the modified wood were then regressed on holocellulose content following partial hydrolysis. All three treatments significantly reduced the holocellulose content in each species, with the greatest reduction obtained in the acid treatment, followed by the alkaline solution treatment and the deionized water treatment, respectively. The changes in holocellulose explained a majority of the variation in mass loss due to treatment and specific modulus, whereas surface free energy was poorly explained by changes in the wood structure. Implications for wood composites manufacturing are discussed.

Conversion of lignocellulosic materials, including wood, to ethanol has become a primary agricultural policy concern. Low-valued small trees from southern hardwood species can provide an excellent feedstock source for biorefineries. These stems are primarily early to mid successional species, such as red oak (*Quercus* spp.), sweetgum (*Liquidambar styraciflua* L.), and yellow-poplar (*Liriodendron tulipifera* L.), among others, that compete with southern pine (*Pinus* spp.) on many sites. Rather than adding cost to their timber investment by applying expensive silvicultural treatments, landowners can have these stems harvested for biofuel conversion.

The refining process, however, completely hydrolyzes the lignocellulosic material to maximize sugar yield by using a combination of extreme temperatures and harsh chemicals. A by-product consisting of mainly lignin, which currently has little commercial value, is primarily burned for energy onsite (Garrote and Parajo 2002). High input costs coupled with low output revenues due to a lack of added value being realized from the conversion process currently leave lignocellulosic ethanol cost prohibitive. Therefore, an alternative lignocellulosic conversion process needs to be investigated to provide added wealth to the landowner, productivity to the logger, and revenue streams to the production facility.

One option would employ relatively low temperatures and chemical concentrations, which would only partially hydrolyze the wood. This would result in forming some hydrolyzed sugars to ferment for conversion to ethanol while leaving behind a modified wood by-product that remains structurally whole rather than being pulped to individual fibers. This by-product could add value to the conversion process as a raw material, with possibly improved properties, for wood composites. However, few studies have been conducted on wood properties following treatment in a heated solution (Hill 2006, Ragauskas et al. 2006).

Wood heated in solution under pressurized conditions undergoes many mechanical, physical, and chemical modifications due to changes in the chemistry of the wood cell wall brought about by hydrolysis. The extractives are the first constituents removed, because they are nonstruc-

tural components of low molecular weight (Parham and Gray 1984). Certain carbohydrates, particularly the hemicelluloses, are also susceptible to chemical reactions and are isolated rather easily from the wood cell wall (Rowell et al. 1988).

Time and temperature are key components in the hydrolysis process, because high temperatures solubilize acidic components in the hemicelluloses of wood (Li et al. 2010). Heating wood in water results in an autohydrolysis, which releases acetic acid by hydrolyzing hemicellulose acetate in the water (Connor 1984). Khrol and Gromov (1976) demonstrated that autohydrolysis at temperatures ranging from 100°C to 180°C altered the chemical composition of wood. The intensity of the transformations increased with the rise in temperature. A rapid first stage was noted as easily hydrolyzed substances, mostly pentosans, were removed by formation of organic acids, causing a reduction of the solution's pH value. A second stage was noted as isolation of other components continued, but at a much slower rate. Little cellulose, though, is extracted below 230°C (Garrote et al. 1999). Furthermore, heating wood in alkaline solutions catalyzes the hydrolysis process as well as lowers degree of polymerization (DP) for cellulose through peeling reactions and random scission (Sjöström 1993), whereas treating wood in acid quickens the decrease in cellulose DP (Winandy and Lebow 2001). Extraction rates tend to be curvilinear, leveling with time (Harris et al. 1958, Khrol and Gromov 1976).

These changes result in lower values for mechanical properties (Thompson 1969), significant weight losses (Paredes et al. 2008), increased dimensional stability (Rowell et al. 1988), and decreased biodegradation due to decay fungi (Howell et al. 2009). Most extractives and hemicelluloses are removed (Mills et al. 2009) as wettability increases (Paredes et al. 2009).

The purpose of the present work was to study the carbohydrate fraction of red oak, sweetgum, and yellow-poplar wood partially hydrolyzed at 150°C for 30 minutes in three treating solutions along with untreated controls. The changes in the carbohydrate fraction, holocellulose, were then related to the resulting mechanical, physical, and surface properties of the modified wood as found in Table 1 (McConnell and Shi 2010, 2011), and their implications for wood composites manufacturing are discussed.

Materials and Methods

Partial hydrolysis treatment

Defect-free yellow-poplar, sweetgum, and red oak lumber, 50 mm thick by 292 mm wide by 2.44 m long, were randomly selected from a local sawmill. The boards were ripped and sawn into miniature beams measuring 3 mm by 15 mm by 150 mm (tangential by radial by longitudinal). Twenty-four samples from each species were randomly selected and allocated to four treatments: 1.0 percent sulfuric acid (H_2SO_4), deionized (DI) water, 1.0 percent sodium hydroxide (NaOH), and untreated controls. Initial moisture content was determined on a subset of randomly selected samples of each species following oven drying at 103°C for 24 hours so that ovendry weights of the test samples before treatment could be estimated.

The miniature beams were DI water saturated under vacuum pressure. Each sample was treated individually in a 2-liter reactor (Parr 4843) at 150°C for 30 minutes in the

Table 1.—Average response values measured following a partial hydrolysis treatment.[a]

Species	Treatment[b]	Specific modulus (GPa)[c]	Mass loss due to treatment (%)	Surface free energy (mJ/m^2)[d]
Red oak	H_2SO_4	18.7*	−33.6*	49.7
	DI water	25.1	0.0	50.4
	NaOH	23.6	−17.0*	47.0
	Control	25.3	−0.4	44.1
Sweetgum	H_2SO_4	14.8	−39.7*	54.7
	DI water	16.3	−7.5	49.6
	NaOH	17.3	−19.4*	45.6
	Control	17.2	−1.5	49.1
Yellow-poplar	H_2SO_4	27.2	−33.3*	56.1
	DI water	24.6	−4.1*	53.2
	NaOH	20.0*	−19.1*	47.5
	Control	25.1	−1.8	50.7

[a] For detailed analyses of these responses, please refer to McConnell and Shi (2010, 2011). An asterisk indicates a significant difference between a treatment and its control for each species using Dunnett's t test ($\alpha = 0.05$).
[b] H_2SO_4 = sulfuric acid; DI = deionized; NaOH = sodium hydroxide.
[c] Specific modulus is defined as modulus of elasticity divided by ovendry density.
[d] Surface free energy values are absolute terms and are not open to statistical comparisons.

designated solution. The untreated controls were only water saturated; they were not placed in the reactor. Each treatment combination was randomly performed daily over 6 days ($n = 24$ per species, $n = 18$ per treatment, $N = 72$). The average pH for each treatment, as determined by pH indicator paper, was 3.5 for H_2SO_4, 6.5 for DI water, and 10.0 for NaOH. The samples were placed in a bath of DI water for 24 hours following treatment. They were removed to a chamber set at 21°C ± 2°C and 41 ± 5 percent relative humidity until attaining a constant weight and then oven dried at 60°C in a convection oven to a constant weight (McConnell and Shi 2010).

Mechanical and physical properties

The samples were weighed and measured for density calculation (ovendry mass and volume). Modulus of elasticity (MOE) was determined on a bending machine according to American Wood Protection Association (AWPA) Standard E23-09 (AWPA 2009b). The span was 120.0 mm, and samples were loaded at a rate of 10.0 mm/min to a deflection of 1.0 mm. Density variations due to species and treatment effects were accounted for by calculating the specific modulus, which was the ratio of MOE over the ovendry density. Mass loss was determined following AWPA Standard E1-09 (AWPA 2009a) and calculated as the percent difference between the estimated ovendry mass before treatment and the actual ovendry mass after treatment. Analysis of variance (ANOVA) was run on specific modulus and mass loss for mean comparisons (McConnell and Shi 2010). The samples were returned to conditions set at 21°C ± 2°C and 41 ± 5 percent relative humidity until attaining a constant weight.

Surface properties

Surface properties were determined by dynamic contact angle (DCA) analysis using a Thermo Cahn DCA 322 by applying the Wilhelmy plate technique in four probe liquids with known surface properties, DI water, α-bromonaphtha-

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lene, formamide, and ethylene glycol. The DCA samples were obtained by planing across the tangential surface of a miniature beam to a target thickness of 0.25 mm, and they were cut to a length of 15.0 mm. The width and thickness of each sample were measured three times with calipers and averaged before each DCA test run. A sample was hung above 80 mL of a probe liquid and counterbalanced with weights to a precision of ± 1.0 mg. The advancing DCA was measured to a depth of 4.0 mm at a rate of 264 μm/s and averaged for each wood-treatment combination. The surface free energies of the wood-treatment combinations were calculated using the geometric mean model based upon the mean contact angle of a wood surface and the known surface tension values of the probe liquids. The surface energy components of the wood surfaces were determined using simple linear regression (McConnell and Shi 2011).

Holocellulose content

The remaining wood material from the miniature beams for each wood-treatment combination was ground in a Wiley mill to a size 20 mesh. Extractive-free wood was prepared following ASTM D1105-96 (American Society for Testing and Materials [ASTM] 1996) with the exception of extracting reagents, which were a 1:1 mixture of methanol and benzene (600 mL in total). A Soxhlet apparatus was used for the reaction, which was allowed to run for 6 hours. The wood meal was placed in a petri dish and left to dry for 24 hours, and then was placed in a sealed plastic bag to equilibrate. The wood meal was analyzed gravimetrically on a wet-chemistry basis for extracted contents and moisture content (total solids). Total solids content was determined after oven drying for 5 hours at 104°C ± 5°C.

Holocellulose was measured in replicate on extractive-free wood (wet-chemistry basis) following ASTM D1104-56 (ASTM 1956). A total of 150 mL of DI water was added to 2.5 g of wood powder. The beaker was heated in a water bath to 75°C. Each hour for 5 hours, 10 drops of glacial acetic acid and 1.5 g of sodium chlorite were added, and the beaker was vigorously stirred. After 5 hours, the solution was filtered through a coarse sintered glass filter using an aspirator. The filtrate was washed with DI water to neutrality and then washed with acetone and left to dry overnight. Holocellulose content was determined gravimetrically after oven drying for 5 hours at 104°C ± 5°C. The reduction in holocellulose content was also calculated as a percentage of the control for each replicate. Results were analyzed using ANOVA, with α = 0.05 for the level of significance. Multiple comparisons were made using Dunnett's t test for each species. Holocellulose content was then correlated to the changes in specific modulus, mass loss due to treatment, and surface free energy of the modified woods using simple linear regression. SAS 9.1.3 software (SAS Institute 2003) was used for all analyses.

Results and Discussion

Summary statistics for the holocellulose content and reduction in holocellulose of extractive-free wood are provided in Table 2. The effect of the treating solutions on the holocellulose content was significant ($P < 0.01$). All treatments significantly lowered the holocellulose content for the three species. An acid treatment produced carbohydrate reductions of at least 10 percent. The H_2SO_4 treatment lowered the holocellulose content the greatest amount in red

Table 2.—Average holocellulose content and average reduction of the holocellulose fraction (coefficients of variation) following treatment.

Species	Treatment[a]	Holocellulose (%)[b]	Reduction (% of control)
Red oak	H_2SO_4	70.1 (0.1)*	13.7
	DI water	78.4 (0.1)*	3.5
	NaOH	74.6 (0.0)*	8.1
	Control	81.2 (0.5)	
Sweetgum	H_2SO_4	63.6 (0.4)*	18.6
	DI water	71.3 (0.0)*	8.8
	NaOH	67.3 (0.7)*	13.9
	Control	78.2 (0.6)	
Yellow-poplar	H_2SO_4	74.4 (0.1)*	10.0
	DI water	76.3 (0.8)*	7.8
	NaOH	73.7 (0.5)*	10.9
	Control	82.7 (0.1)	

[a] H_2SO_4 = sulfuric acid; DI = deionized; NaOH = sodium hydroxide.
[b] Minimum significant difference for red oak = 1.27 percent, minimum significant difference for sweetgum = 2.19 percent, and minimum significant difference for yellow-poplar = 2.06 percent. An asterisk indicates a significant difference between a treatment and its control for each species using Dunnett's t test (α = 0.05).

oak and sweetgum, whereas the NaOH treatment produced the lowest value in yellow-poplar. Sweetgum retained less holocellulose following each treatment compared with red oak and yellow-poplar.

Of the results analyzed in Table 1, the average holocellulose content of the wood species following treatment explained a majority of the variation in mean specific modulus and mass loss due to treatment; coefficients of determination (R^2) were 0.61 for mass loss (Fig. 1) and 0.52 for specific modulus (Fig. 2). The regressions for both of these responses were significant (specific modulus, $P < 0.01$; mass loss, $P < 0.01$). The changes in average holocellulose poorly explained surface free energy ($R^2 = 0.04$, $P = 0.52$).

Treating wood in a heated environment alters the chemical structure of the wood cell wall, which in turn changes the ultrastructure of the wood material due to the degradation of structural components (Baechler 1954, Biermann et al. 1984, Repellin and Guyonnet 2005, Mills et al. 2009). The extraction of soluble components further affects the wood's ability to retain its original identity, because changes in color, mass, volume, and tenacity, among others, take place (Wangaard 1966, Hill 2006, McConnell and Shi 2010). Modifying the mass and volume subsequently alters the density of the treated wood, perhaps the most important predictor for mechanical properties of both solid wood and composite panels (Kellog and Ifju 1962, Blankenhorn et al. 1989). Changes in the toughness of solid wood, for instance, were significantly dependent upon the changes in holocellulose content (Davis and Thompson 1964). Modulus of rupture and work-to-maximum load are also dependent upon the holocellulose fraction (Wangaard 1966). Analysis of the wood surface revealed alkaline aromatic extractives are predominant in hardwoods, and this has a great influence on the acid–base interaction component of the total surface free energy (Gardner 1996). The slightly acidic water solution, along with the more acidic H_2SO_4, neutralized the wood surface. The NaOH, while removing the extractives, increased the alkalinity of the
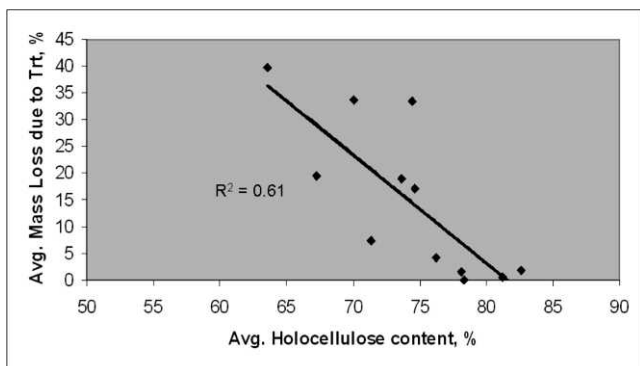
Figure 1.—Regression explaining the mass loss due to treatment based upon holocellulose content following treatment.

wood surface and lowered the surface free energy (McConnell and Shi 2011).

These results suggest no single explanatory factor for responses by these southern hardwood species to a partial hydrolysis in the three solutions tested. The regressions for mass loss due to treatment and specific modulus were significant, but neither showed a particularly strong relationship. This suggests other factors, such as the following, may be at work.

First, the species examined in the present work have naturally different holocellulose contents. Pentosan content and wood degradation are directly related (Kass et al. 1970). Petterson (1984) and Hergert et al. (1977) stated that the pentosan hemicellulose content of sweetgum is higher than that of either red oak or yellow-poplar. Also, hemicelluloses are less resistant to hydrolysis compared with other structural components (Thompson 1969), and the presence of an acid or alkaline catalyst can hasten the degradation of the hemicellulose fraction (Hill 2006). Second, Wangaard (1966) suggested lignin content played a significant role in strength retention for wood subjected to an acid treatment. Hergert et al. (1977) reported that yellow-poplar had a lignin content of 30.3 percent and that sweetgum and red oak had lignin contents of 24.7 and 23.3 percent, respectively. Third, very little relationship existed between holocellulose content and surface free energy, because the coefficient of determination was near zero. This may be due, in part, to the nonstructural extractives; Gardner (1996) concluded that extractives content was a primary indicator of surface free energy.
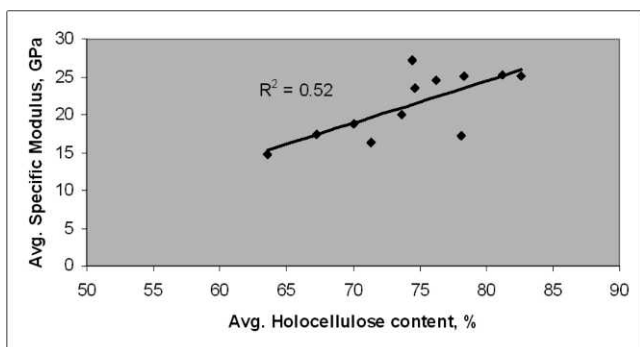

Figure 2.—Regression explaining specific modulus based upon holocellulose content following treatment.

Providing both a biofuel feedstock and a raw material for wood composites would require a partial hydrolysis to lower the mass of the wood material and, with that, the specific modulus as well as increase the surface free energy while separating a significant amount of wood sugars for ethanol conversion. Wood composite products offer an economically valuable avenue for underused species and undersized timber. This is not a simple matter of wood utilization, however, because compaction and adhesion issues currently limit the use of hardwoods in these products (Carll 1997). To overcome these shortcomings, wood modification has long been looked at as a means of diversifying the raw material base by treating wood with heat and/or chemicals (Youngquist et al. 1986). Blankenhorn et al. (1989), for example, examined chemically treating red oak with acetic acid to enhance its properties for flakeboard manufacturing. Mass loss in flakes was determined to be a controllable factor in chemical modification. Flakes treated with 2 percent acetic acid did not reduce press closing time, but mechanical properties were not significantly different than those of the control.

The results of the present research suggest no one treatment can achieve the above requirements if a composite mill were to process a mixed furnish consisting of these hardwoods. A DI water treatment produced desirable results for available carbohydrates following treatment (Table 2) yet little significant changes in wood properties (Table 1). The NaOH treatment lowered surface free energy in sweetgum and yellow-poplar, which could be problematic for wood adhesion. Also, no significant reduction in specific modulus was observed in red oak or sweetgum following NaOH treatment. Of the three treatments tested, H_2SO_4 produced significant mass losses, a significant amount of potential carbohydrates for fuel conversion, and an increase in the surface free energy of at least 10 percent for each species. Only red oak's reduction of specific modulus was of statistical significance. Sweetgum's specific modulus was the lowest, although not significantly, in the H_2SO_4 treatment; yellow-poplar's specific modulus experienced a small, insignificant increase.

Conclusions

Better utilization of our timber resources, particularly the small-diameter hardwoods that currently have little or no marketability, would benefit not only production forestry (landowner, logger, and mill) but also the rural economies in which each segment operates. Partially hydrolyzing underutilized hardwood stems could add value to the lignocellulosic ethanol conversion process by producing not only carbohydrates for fuel but also a structurally whole, woody by-product with the potential to be a desirable wood composite raw material. The holocellulose contents of red oak, sweetgum, and yellow-poplar partially hydrolyzed in three solutions at 150°C for 30 minutes were determined and correlated to mechanical, physical, and surface properties of the modified woods. All treatments significantly reduced the holocellulose content in each species. The greatest reduction in holocellulose was obtained in the acid treatment, followed by the alkaline solution and the DI water treatment, respectively. With the exception of yellow-poplar specific modulus, the H_2SO_4 treatment produced the wood property changes needed for southern hardwoods to be used in wood composites. Water extracted a significant amount of holocellulose in each species but only minimally changed

any of the residual wood properties. The NaOH solution negatively affected the surface properties. Overall, a majority of the variation in mass loss caused by the treatment and the specific modulus was explained by changes in the holocellulose content following partial hydrolysis. Surface free energy was not explained by structural changes to the wood.

These property evaluations are an important first step, but much work remains to be done. Economic analyses need to be conducted at each stage of production forestry to determine the viability of the fundamental hypothesis for this research. This could include landowner, harvest, and haul costs as well as the opportunity costs of constructing a biorefinery onsite. Pilot-scale industrial operations research needs to be directed toward recovery of the treating chemical and the extracted carbohydrates. The logical place for a treating vessel would be between the primary breakdown of the logs and the dryers; thus, time studies of material flow are needed. Comprehensive quality-assurance testing of pressed panels or billets should investigate the various factors involved in the manufacturing process, such as wood material geometry, alignment, drying, resin and additives, and press cycling, so that costs are kept to a minimum while value is added to the extraction process. Environmental compliance studies on emissions and chemical disposal also need to be conducted.

Acknowledgments

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