

Surface Energy Characterization of Three Partially Hydrolyzed Hardwood Species Determined by Dynamic Contact Angle Analysis

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The effects of a partial hydrolysis treatment on the surface energies of three southern hardwood species, red oak, sweetgum, and yellow-poplar were examined. Miniature beams machined to $3 \times 15 \times 150$ mm ($t \times r \times l$) were water-saturated and subjected to a partial hydrolysis at 150°C for 30 min in 1% sulfuric acid, water, or 1% sodium hydroxide solutions. Untreated wood beams were used as controls. Dynamic contact angle specimens were planed from the beams to a thickness of 0.25 mm and cut to a length of 15 mm for analysis via the Wilhelmy plate technique. Surface energies for the wood/treatment combinations were calculated using the geometric mean procedure. Results indicated that acid and water treatments improved the wettability for all species. Alkaline treatment effects were species-specific. All treatments improved the surface energy of red oak. The dispersive forces accounted for the majority of the surface energies.

Keywords: Dynamic contact angle; Hardwood; Partial hydrolysis; Surface energy

1. INTRODUCTION

The primary timber source for strand-based wood composites in the southern United States is southern pine (*Pinus* spp.), but the increasing demand for composite products is straining this feedstock supply. Hardwoods, such as yellow-poplar (*Liriodendron tulipifera* L.), sweetgum (*Liquidambar styraciflua* L.), and red oak (*Quercus* spp.), associated

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with pines on sites across the region, are plentiful and inexpensive. However, the extractives in these species, such as resin, carbohydrate metabolites, etc., affect their adhesion performance [1]. These extractives are generally of low molecular weight and independent of the lignocellulosic structure. Migration of these extractives onto the wood surface contribute to surface deactivation, compromising the wood-adhesive bond during pressing [2,3]. Oak, for example, prematurely gels phenol formaldehyde (PF) resin due to the release of acidic extractives [4]. Low compressive pressures result when pressing high-density hardwoods, with extractives content and hardwood density directly related [5]. This is due to the thinner cell walls and greater lumen volumes of low density species being compressed more than high-density species at the same pressure [6]. Utilizing mixed hardwood furnish also results in a lower compaction ratio (the panel density over wood species density) for the composites because of the higher density for many hardwood species. Irreversible thickness swelling can thus occur, first upon the press opening, and second when the composite is exposed to moisture. Mechanical properties also suffer due to the increased presence of void spaces.

Modifying wood by chemical processes dates back decades with large scale processing of wood sugars for human and livestock consumption during World War II in Germany [7]. Research using this technology has shifted to alternative fuel production in recent years. The utilization of existing infrastructure within the forest products industry to convert small-diameter hardwood species into ethanol has been reviewed [8]. Many separation processes have been investigated, including acid and alkaline hydrolysis, autohydrolysis, and steam explosion [9–11]. A biorefinery in the classical sense, though, requires harsh conditions at high temperatures, resulting in the complete breakdown of the wood material into its rudimentary carbohydrate components for sugar harvesting and chemical separation [12]. However, performing a less severe treatment at lower temperatures may only partially hydrolyze the wood, removing the extractives followed by easily extracted structural components such as pentosan hemicelluloses for fuel conversion, while leaving the residual material structurally whole. This modified wood material may demonstrate an improved adhesive wetting performance for manufacturing strand-based wood composites.

Past research has shown that treating wood with heat and chemicals affects wetting. The interactions of PF resin and southern yellow pine were investigated [13]. One test involved treating pine with 1% cetyl alcohol in methanol and a PF resin of low surface tension ($\gamma = 53.4 \text{ mN/m}$) in methanol. A PF resin treatment lowered the

contact angle compared with the control, while an alcohol treatment increased the contact angle due to the hydrogen bonding with the hydroxyl groups on the cellulose chain. Springwood had greater wetting potential than summerwood. Paredes *et al.* [14] investigated the surface properties of red maple following hot water extractions at 160°C for 0, 45, and 90 minutes. Contact angles were determined in water, ethylene glycol, and diiodomethane. Specimens treated for at least 45 minutes showed a 0° contact angle in each probe liquid, resulting in increased surface energies. The longer treatment times resulted in greater removal of both extractives and hemicelluloses, thus increasing the acid/base characteristics of the wood. The alkaline characteristics showed their largest values at the lowest treatment time, decreasing with time as acetyls were cleaved from the hemicelluloses.

The determining factor for the quality of wood composites is the wood–adhesive bond [15]. For wood adhesion to be successful, the adhesive must adequately wet the wood surface. Penetration into the micropore structures of the wood cell wall provides intimate contact between the two wood elements at a molecular level, which is critical for adhesive bonding strength and the product's durability [16]. Producing higher compaction ratios results in more efficient wood contact and adhesive distribution, as more penetration would increase bond effectiveness between the wood and adhesive [17]. Further, swelling due to spring-back, which weakens the wood-adhesive bond, would be minimized [6].

The goals of this study were to determine the dynamic contact angles of miniature beam specimens of three species, red oak, sweetgum, and yellow-poplar, after partial hydrolysis. The Wilhelmy plate technique was utilized with four probe liquids. The surface energies of the treated woods were then calculated by the geometric mean procedure and compared with untreated controls.

2. MATERIALS AND METHODS

2.1. Materials

Rough-cut red oak, sweetgum, and yellow-poplar lumber were obtained from a local sawmill. The red oak and sweetgum lumber had been freshly sawn within the previous day while the yellow-poplar had been air-drying for some time. The rough lumber size was 50 mm thick by 292 mm wide by 2.44 m long. Care was taken to select wood free of sawing and drying defects. Five boards free of any visual defects were randomly selected and stored at a target temperature of 2°C.

One board was randomly selected from each species to minimize sample variation and processed into miniature beams measuring

3 mm × 15 mm × 150 mm (tangential × radial × longitudinal). The initial specific gravity (oven-dry basis) and moisture content of the lumber were calculated from a subset and averaged for each species. Samples (n = 54) were measured for volume calculation then oven-dried at 103 ± 3°C for 24 hours (Table 1).

All samples were fully saturated in deionized water under a vacuum pressure of 85 kPa. Chemical treatment with 1% sulfuric acid (H₂SO₄, Fisher Scientific, Fairlawn, NJ, USA), deionized water, and 1% sodium hydroxide (NaOH, Fisher Scientific, Fair Lawn, NJ, USA) was conducted using a Parr (Moline, IL, USA) 4843 2-L Pressure Reactor. The vessel was filled with 1,700 mL of solution, and a miniature beam was immersed. Glass fiber was placed over the miniature beam sample to ensure a full immersion in the liquid. Time measurement began at the point in which the reactor reached 150°C; ramp up time for the reactor was 45 min, approximately 3°C per min. After 30 min had elapsed the vessel was cooled and the pressure was then released. The specimen was washed with deionized water and placed in a bath of distilled water for 24 h. The reactor was thoroughly cleaned after each run. A blank run of only the next solution was conducted between treatments to prevent contamination by the previous species/solution combination. Six replicates per treatment combination were performed (3 species × 4 treatments × 6 replicates, n = 72). Mass loss and specific gravity following treatment were determined in a prior experiment (Table 1). The average pH was 3.5 for the acid

TABLE 1 Average Values (Standard Deviation) Pre- and Post-Treatment. Post-Treatment Values were Based on Oven-Dry Weights and Volumes [18]

Species	Treatment	Pre-treatment		Post-treatment	
		Specific gravity	Moisture content, %	Specific gravity	Mass loss, %
Oak	Acid	0.62 (0.01)	55.6 (8.67)	0.72 (0.06)	-33.59 (1.83)
	Water			0.76 (0.01)	0.02 (3.31)
	Base			0.87 (0.09)	-16.98 (1.72)
	Control			0.69 (0.01)	-0.43 (6.00)
Sweetgum	Acid	0.55 (0.01)	44.8 (5.14)	0.58 (0.04)	-39.69 (2.91)
	Water			0.68 (0.03)	-7.45 (2.87)
	Base			0.71 (0.04)	-19.39 (7.66)
	Control			0.67 (0.03)	-1.47 (3.56)
Yellow-poplar	Acid	0.39 (0.02)	20.13 (0.55)	0.35 (0.03)	-33.31 (1.06)
	Water			0.40 (0.01)	-4.13 (0.57)
	Base			0.48 (0.02)	-19.05 (1.34)
	Control			0.41 (0.02)	-1.80 (1.44)

solution, 6.5 for water, and 10.0 for the alkaline solution as determined by pH indicator paper [18].

Following treatment, the miniature beams were placed in a conditioning chamber at $21 \pm 2^\circ\text{C}$ and $41 \pm 5\%$ relative humidity until attaining a constant weight. Dynamic contact angle samples were planed from the beams with a Stanley (New Britain, CT, USA) No. 90 FJ Bullnose plane to a target thickness of 0.25 mm (radial) and cut to a target length of 15 mm (longitudinal). The width (tangential) varied among the species and treatments as some structural components were extracted due to the partial hydrolysis of the wood [18]. The actual dimensions of each specimen were measured three times using calipers, averaged, and recorded at the time of testing.

2.2. Methods

Contact angle and surface free energy are usually used to evaluate the wettability of materials [19]. Their relationship was originally described by Young's [20] equation

$$\gamma_S - \gamma_{SL} = \gamma_L * \cos \theta. \quad (1)$$

where γ_S represents the surface free energy of the solid; γ_{SL} represents the surface free energy of the solid – liquid; γ_L represents the surface tension of the liquid; θ represents the contact angle.

Initial studies on wettability and contact angle measurements involved placing a drop of liquid onto the wood surface and generally measured only the instantaneous or equilibrium contact angles [21]. However, due to the wood's porous structure and surface roughness, more accurate measurements to describe the wetting process were needed [18]. The dynamic contact angle measured by the Wilhelmy plate technique is much more sensitive to predicting perimeter changes in the wood due to its accounting of the intricacies of the wood surface on a microscopic scale [22]. The downward force of a wood sample hanging perpendicular to the surface of the liquid is measured. When the wood initially contacts the liquid, the equilibrated force can be expressed as

$$F = \gamma_L * P * \cos \theta. \quad (2)$$

where F is the force on the object, γ_L is the surface tension of the liquid, P is the wetted perimeter, and θ is the contact angle between the solid and the liquid [23]. When the sample is partially immersed in the liquid, a buoyancy correction is included in the equation. Thus,

$$F = \gamma_L * P * \cos \theta - (\rho * V). \quad (3)$$

where ρ is the density of the liquid and V is the volume of the solid.

A Thermo Cahn (Newington, NH, USA) DCA 322 was used for the dynamic contact angle measurement. Four probe liquids, α -bromonaphthalene, ethylene glycol, formamide, and deionized water, with known surface tension components were used (Table 2) [24]. The deionized water was filtered using a Thermo Scientific EASYPure[®] RoDi (Dubuque, IA, USA) filtration system. About eighty milliliters of probe liquid were poured into a beaker and placed on a moving stage mechanism. The sample was clipped and hung perpendicular to the surface of the liquid. It was then balanced to within ± 1 mg by adding a stirrup and counterweights (Fig. 1). When the balance became stationary, the test was initiated. The stage was operated by a motor, rising at 264 microns per second. Force and depth data were collected to 4.0 mm upon sample and liquid contact at the zero depth of immersion. The advancing dynamic contact angle was calculated through WinDCA software (Newington, NH, USA).

A combination of Young's equation [20], Good's and Girifalco's geometric mean law [25], and Fowkes' equation [26] describing the dispersive and polar components of surface energy was used to determine the surface tension of each wood/treatment combination:

$$\frac{(1 + \cos \theta) * \gamma_L}{2 * (\gamma_L^d)^{0.5}} = (\gamma_S^d)^{0.5} + (\gamma_S^p)^{0.5} * \left(\frac{\gamma_L^p}{\gamma_L^d} \right)^{0.5} \quad (4)$$

where θ represented the mean contact angle in the liquid, γ_L represented the surface tension of the liquid, γ_L^d and γ_S^d represented the surface free energy from London dispersion forces of the liquid and the wood, and γ_L^p and γ_S^p represented the surface free energy from the dipole-dipole interactions of the liquid and wood. The unknown parameters of each wood/treatment combination, γ_S^d and γ_S^p , were calculated using simultaneous equations for each probe liquid [27,28]. The simultaneous equations were solved using simple linear

TABLE 2 Surface Tension and Components (mJ/M²) of the Probe Liquids [23]

Probe liquid	γ_L	γ_L^d	γ_L^p
α -Bromonaphthalene ^a	44.4	44.4	0.0
Ethylene Glycol ^a	48.0	29.0	19.0
Formamide ^b	58.0	39.0	19.0
Deionized Water	72.8	21.8	51.0

^aFisher Scientific, Fair Lawn, NJ, USA.

^bArcos Organics, Morris Plains, NJ, USA.

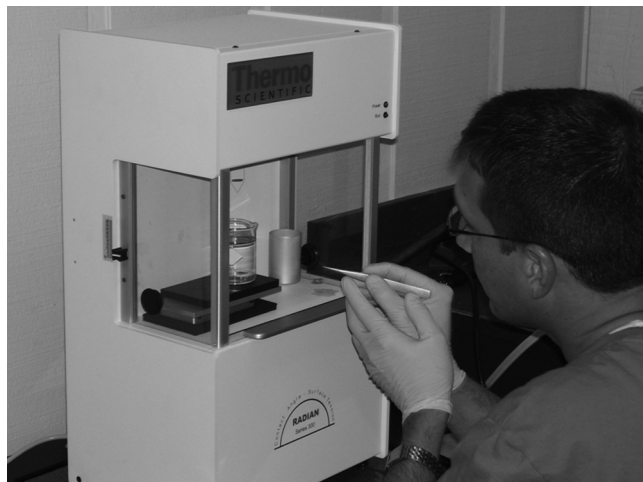


FIGURE 1 Counterbalancing the Thermo Cahn DCA 322.

regression in SAS[®] 9.1.3 [29]. The model used for the analysis was

$$Y = \beta_0 + \beta_1 X + \varepsilon. \quad (5)$$

where Y represented the dependent variable $\frac{(1+\cos\theta)\gamma_L}{2(\gamma_S^d)^{0.5}}$, x represented the independent variable $\left(\frac{\gamma_S^p}{\gamma_S^d}\right)^{0.5}$, β_0 represented the intercept $(\gamma_S^d)^{0.5}$, β_1 represented the slope $(\gamma_S^p)^{0.5}$, and ε represented the error of the model. The intercept and slope were squared to determine the dispersive and polar forces. The solid surface energy, γ_S , was then calculated by

$$\gamma_S = (\gamma_S^d) + (\gamma_S^p). \quad (6)$$

3. RESULTS AND DISCUSSION

The measured advancing contact angles of the treated specimens are listed in Table 3 and an example contact angle run is shown in Fig. 2. An increase in friability was generally observed on the treated wood samples compared with the controls. The presence of an acid or caustic in a treating solution accelerates wood degradation, with acid being the more severe of the two. This degradation may have contributed to the variation in the acid treatments. The water treatment became a weak acid over time as acetyl groups are hydrolyzed, resulting in some autohydrolysis of hemicelluloses by the acetic acid.

TABLE 3 Advancing Contact Angles of the Treatment Combinations in Four Probe Liquids

Probe liquid				
Average contact angle (standard deviation)				
Trt Combination	Water	Formamide	α -Bromonaphthalene	Ethylene glycol
Red Oak/Acid	80.6 (6.3)	25.0 (23.9)	29.9 (11.6)	19.3 (17.8)
Red Oak/Water	49.9 (10.0)	37.4 (6.4)	28.3 (7.0)	32.4 (4.8)
Red Oak/Base	51.0 (6.7)	46.5 (5.1)	37.9 (8.2)	39.9 (7.3)
Red Oak/Control	64.0 (10.0)	43.6 (1.7)	36.6 (6.2)	39.2 (2.9)
Sweetgum/Acid	80.0 (5.9)	9.0 (15.4)	13.0 (14.7)	8.1 (11.4)
Sweetgum/Water	50.2 (3.8)	37.1 (6.67)	30.6 (5.4)	36.5 (6.6)
Sweetgum/Base	55.6 (2.9)	45.9 (6.7)	37.9 (5.1)	40.0 (5.9)
Sweetgum/Control	51.0 (14.3)	38.8 (3.7)	31.7 (8.6)	36.3 (3.6)
Yellow-poplar/Acid	52.8 (15.4)	3.9 (9.6)	0.0 (0.0)	0.0 (0.0)
Yellow-poplar-Water	48.3 (12.0)	30.8 (5.9)	16.6 (12.3)	26.0 (10.9)
Yellow-poplar/Base	54.8 (13.0)	42.9 (5.0)	32.0 (11.1)	35.0 (4.9)
Yellow-poplar/Control	48.4 (10.3)	32.4 (3.8)	30.3 (4.8)	37.1 (3.4)

The calculated results of solid surface energy components, γ_S^d and γ_S^p , and the total surface energy, γ_S , are listed in Table 4, where the total surface energies were increased for all three hardwood species after acid and water extraction. For red oak, the total surface energy was increased 13% from 44.1 mJ/M² to 49.7 mJ/M² after acid hydrolysis and 14% to 50.4 mJ/M² after water hydrolysis. For sweetgum, the total surface energy was increased 11% from 49.1 mJ/M² to 54.7 mJ/M² after acid hydrolysis and 1% to 49.6 mJ/M² after water hydrolysis. For yellow-poplar, the total surface energy was increased 11% from 50.7 mJ/M² to 56.1 mJ/M² after acid hydrolysis and 5% to 53.2 mJ/M² after water hydrolysis. The total surface energy of red oak increased after alkaline hydrolysis 7% to 47.0 mJ/M² while sweetgum decreased 7% to 45.6 mJ/M² and yellow-poplar decreased 6% to 47.5 mJ/M². The acid and water treatments increased the total surface energies across the species an average of 12% and 7%, respectively. The increased surface energies indicate that the acid and water treatments should improve the adhesive wettability on the species, in turn improving the wood/adhesive bond.

The two surface energy components, polar and dispersive forces, negatively and significantly correlated with one another across the treatments ($R^2 = 0.79$, $p < 0.01$, Fig. 3), with the dispersive component accounting for most of the total surface energy. As the dispersive forces increased, the polar forces decreased. The highest improvements on the dispersive component were obtained by the acid treatment. Caustic

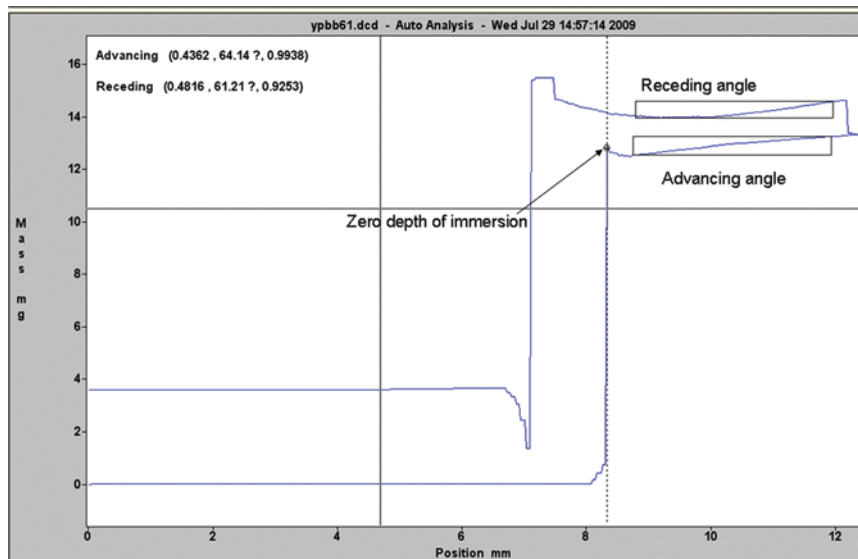


FIGURE 2 Dynamic contact angle run of yellow-poplar/base in α -bromonaphthalene. The x-axis represents the height of the moving stage while the y-axis represents the measured force of the solid-liquid interaction. The results for the advancing angles in the upper left corner are cosine of the contact angle (θ), the contact angle (θ), and the R^2 of the regression line fit to the data for buoyancy correction. Only the advancing contact angle was utilized for calculating the surface free energy.

TABLE 4 Total Surface Energy (mJ/M^2) and its Components Based on Regression Analysis of Four Probe Liquids

Treatment combination	γ_S^d	γ_S^p	γ_S
Red Oak/Acid	46.4	3.4	49.7
Red Oak/Water	32.1	18.2	50.4
Red Oak/Base	27.6	19.4	47.0
Red Oak/Control	32.6	11.5	44.1
Sweetgum/Acid	51.9	2.7	54.7
Sweetgum/Water	31.3	18.3	49.6
Sweetgum/Base	29.0	16.6	45.6
Sweetgum/Control	31.0	18.1	49.1
Yellow-poplar/Acid	41.8	14.4	56.1
Yellow-poplar/Water	35.5	17.6	53.2
Yellow-poplar/Base	31.5	16.0	47.5
Yellow-poplar/Control	31.5	19.2	50.7

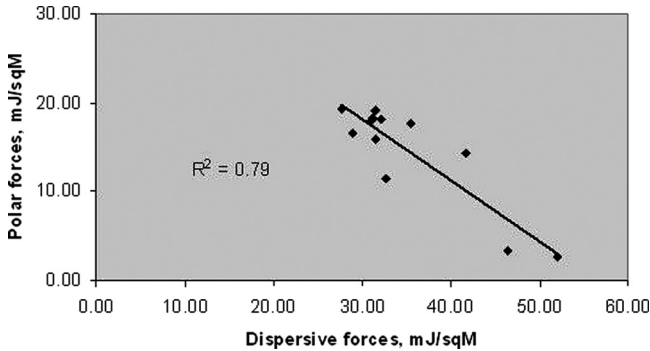


FIGURE 3 Plot of polar *versus* dispersive forces for the twelve wood/treatment combinations.

treatment generally did not improve the dispersive components of the treated wood. The acid treatment notably reduced the polar component for each species, with a 70% reduction for red oak from 11.5 to 3.4 mJ/M², an 85% reduction for sweetgum from 18.1 to 2.7 mJ/M², and a 25% reduction from 19.2 to 14.4 mJ/M² for yellow-poplar. The water and base treatments increased the polar component for red oak, (water – 58% and base – 69%), decreased it for yellow-poplar (water – 8% and base – 17%), and mixed results were found for sweetgum.

Wood is heterogeneous in its chemical composition both between and within species. The pH of most woods is slightly acidic [red oak – 4.9, sweetgum – 5.3, yellow-poplar – 5.4] [30]. However, the surface chemistry reveals that alkaline aromatic compounds are predominant in wood. Gardner [27] concluded that the acid-base interaction component of the total surface energy of six hardwoods was dominated by the basic constituent due to the presence of aromatic compounds. The surface chemistry of the woods tended to exhibit an alkaline pH due to the predominance of electron-donating sites contained within the wood extractives, even though the woods in the bulk were slightly acidic. While red oak had a pH of 4.67 in bulk form, its surface was dominated by aromatics. The phenol content in red oak heartwood is high [30]. Phenolic glycosides are abundant in sweetgum along with cinnamic acid-containing storax [31]. Yellow-poplar contains high amounts of alkaloids and sesquiterpenes. Shi *et al.* [28] found similar results for wood fibers consisting of 75% aspen and 25% assorted hardwoods. De Meijer *et al.* [32] concluded likewise for spruce and meranti.

The sulfuric acid treatments would increase the wood surface energy by neutralizing the surface of the wood. The water solutions

generally become more acidic as well as acetic acid is released during the autohydrolysis process, which, in turn, leads to further acetic acid formation [33]. Although sodium hydroxide hydrolysis initially increases wetting by swelling the wood cell wall [34], the effect of the sodium hydroxide treatment on the already alkaline surface worked to lower the surface energy for sweetgum and yellow-poplar due to the degradation of the cellular structure upon drying [35]. Red oak contains high amounts of acidic extractives which contribute to poor adhesive bonding [36]. Sodium hydroxide had a neutralizing effect on those extractives, which would explain why an alkaline treatment increased the surface energy of red oak. The acid-treated samples, particularly yellow-poplar, had a high degree of surface roughness, which contributed to an increased wetting performance [37].

4. CONCLUSIONS

Contact angles of four probe liquids on three species treated in three solutions (1% sulfuric acid, water, and 1% sodium hydroxide) were compared with the untreated controls. The contact angles of yellow-poplar in acid were generally lower than that of the other treatments, likely due to the friability and surface roughness of the samples. Acid-treated samples suffered some degradation, contributing to the variation within this treatment. Surface energy values were calculated for each species/treatment combination and compared with the controls. The acid treatment improved the dispersive component and reduced the polar component in each species. The total surface energy of red oak was consistently increased by extraction in both alkaline and acidic solutions. The total surface energy of sweetgum was improved by the acid treatment, while those of yellow-poplar were increased by both acid and water treatment solutions. Acid and water treatments likely increased the surface energy values by neutralizing the wood surface *via* extraction of soluble aromatic compounds. The alkaline treatment lowered the surface energy values of sweetgum and yellow-poplar. Dispersive forces were the large contributors to the surface energies of the woods. Partially hydrolyzing these hardwoods in acid or water has the potential to improve wood adhesion for strand-based composites manufacturing as the surface energies improved when employing these treatments.

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