POTENTIAL OF NATURAL-ORIGIN LOBLOLLY PINE TREE FRACTIONS AS A BIOENERGY FEEDSTOCK[1]

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Abstract. Chemical characterization was performed on 10 different samples of loblolly pine (*Pinus taeda* L.), representing the various woody components of trees (bole, slab, tops and branches, and precommercial stem-only) harvested from two naturally regenerated forests in southern Arkansas. Ultimate analysis, proximate analysis using thermogravimetry, and the energy content of the samples were determined to help evaluate their bioenergy utility. Elemental analysis revealed no significant differences between the pine tree fractions, whereas differences were observed in the proximate analysis, particularly in regard to the fixed carbon content. Generally, proximate analyses did not show significant differences between the slabwood and bolewood samples, although the "tops and branches" and "whole stem" samples contained the lowest volatile matter amounts and the greatest amounts of fixed carbon and ash content. In terms of the calorific value, the "tops and limbs" sample reported the lowest energy content, whereas the "whole stem" sample was among the highest reported value with statistical significance. These results indicate that whole stem samples may be an attractive prospect for bioenergy applications such as gasification, pelletization, and combustion, owing to favorable heating content values and relatively low ash content. Although a number of logistical challenges exist in their acquisition and processing, slabs, topwood, and branches offer opportunities for bioenergy applications that can increase the utilization of forest residues without threatening more traditional uses of wood in lumber, panels, and paper. Finally, we then briefly consider the silvicultural implications of these results for naturally regenerated southern pine–dominated forests.

Keywords: Loblolly pine, bioenergy, chemical characterization, forest residues, thinnings.

INTRODUCTION

According to the most recent statistics, southern conifer species, primarily loblolly (*Pinus taeda* L.), shortleaf (*Pinus echinata* Mill.), longleaf (*Pinus palustris* Mill.), and slash (*Pinus elliottii* Engelm.) pines, cover slightly more than 280,000 km^2 in the eastern United States and account for more than 60% of US and about 12% of global industrial wood production (Johnson et al 2009; Smith et al 2009). Loblolly and shortleaf pine forests alone cover 222,000 km^2, comprising more than 50% of the softwood-dominated forests and nearly 15% of all forests in the eastern half of the United States (Smith et al 2009). Such preeminence, coupled with the abundance of accessible, privately owned forests, a generally utilitarian approach to land stewardship, and the rapid growth of a wood-pellet industry strongly suggest that these southern pine forests will play a major role in the future of global bioenergy resources (Eisenbies et al 2009; Galik et al 2009; Alavalapati et al 2013; Goh et al 2013).

Whereas conventional outputs, such as lumber, panels, plup, and paper, are expected to remain the highest value–added products from southern pine forests, underutilized components and residues may offer bioenergy alternatives (Frederick et al 2008; Eisenbies et al 2009; Galik et al 2009). For example, logging slash represents an attractive, largely unused (if sometimes challenging) source of biomass (Greene et al 2014). Globally, Parikka (2004) estimated that ~60% of the total harvested tree is left at the site to decay or used during logging (eg corduroy road) and then discarded. This represents at least 30 EJ of potential bioenergy that could be derived by large-scale use of sustainably harvested forest residues (Heinimö and Junginger 2009), assuming the economics and the logistics allow their widespread application in commercial bioenergy production. Redirecting existing wood residue streams also

presents additional bioenergy options. Parikka (2004) also reported that sawmilling operations around the globe generate residues (45-55% of log input) in the form of slabs and edgings (15-32%), which often find alternative use as low-cost building materials, packaging and mulch, and as feedstock for the pulp and paper industry. These byproducts of the forest products industry (especially sawdust, shavings, trimmings, and other unused slabwood) could easily be converted into pellets, although much of this postprocessing residue is already used for heat, power, and other value-added products (Milota et al 2005).

The conversion of various wood residues into energy via combustion and pelletization represents currently available technologies, yet relatively low returns have limited their development. Next generation biofuels and wood-based chemicals have garnered growing interest, but a number of technological and logistical issues remain in operational-scale implementation (Frederick et al 2008; Elder et al 2011; Greene et al 2014). Currently, the extraction of energy and chemical value from biomass sources requires the adoption of technologies that are primarily divided into biochemical and thermochemical processes (Wright and Brown 2007; Sims et al 2010). Biochemical conversions produce ethanol from the hydrolysis and fermentation of sugars and require relatively pure feedstocks and pretreatments to achieve adequate efficiency. By contrast, thermochemical conversions including combustion, gasification, and pyrolysis can use mixed feedstocks (Foust et al 2009) and are robust technologies with established research that can ultimately be used for the production of power, liquid fuels, and other chemicals.

Regardless of the bioenergy processing technology applied, there are concerns that the environmental impacts related to the collection and processing of forest-based biomass may be unacceptably detrimental, especially if diverse natural-origin forests are converted to short-rotation monospecific plantations of exotic species (Eisenbies et al 2009; Hinchee et al 2009; Abt and Abt 2012; Evans et al 2013; Quinn et al 2014). To date, most work considering bioenergy feedstocks in southern pine–dominated stands has concentrated on residues from planted loblolly pine (eg Smith et al 2009; Greene et al 2014). More information is needed regarding the nature of the feedstocks from naturally regenerated southern pine forests to determine their utility for advanced biofuels and wood chemicals—if these feedstocks are acceptable, then they may present additional revenue opportunities to silviculturists seeking to avoid further conversions of naturally regenerated southern pine forests to loblolly pine plantations.

Hence, our study examines wood components (merchantable bolewood, slabwood, tops and branches from sawtimber-sized trees, and stem-only from precommercial-sized trees) of natural-origin loblolly pine from two sites in Arkansas. The samples were characterized using thermochemical methods to determine their utility for energy generation and to determine if there were differences in these properties between wood components and between these two naturally regenerated pine stands.

MATERIALS AND METHODS

Biomass Feedstock Collection

Samples for this study were obtained from the US Forest Service's Crossett Experimental Forest (Ashley County) and the University of Arkansas Southwest Research and Extension Center's Hope Experiment Station (Hempstead County) in the Upper West Gulf Coastal Plain of southern Arkansas. The samples from the Crossett Experimental Forest consisted of three replicates of bolewood (CEFBW01, CEFBW02, and CEFBW03), three replicates of slabwood (CEFSW01, CEFSW02, and CEFSW03), and a composite whole stem sample (CEFWT01). The slab (CEFSW01-03) and bolewood (CEFBW01-03) samples from the Crossett Experimental Forest were composites of six large loblolly pines felled in 2011 in two pine-dominated stands (three trees from each 16-ha compartment). Managed continuously using uneven-aged silvicultural practices since 1937, these stands (the Good and Poor Farm Forestry Forties) have long produced high-quality pine sawtimber (Bragg and Guldin 2015) and limited quantities of pulpwood. The loblolly pines chosen

to represent this type of feedstock ranged from 40 to 56 cm in diameter at breast height (dbh) and were between 60 and 80 yr old.

The composite whole-stem sample from the Crossett Experimental Forest was generated by felling and combining more than 20 small-diameter (7-15 cm dbh; considered precommercial to marginally commercial) loblolly pines chosen from other even-aged compartments (ie not the Good and Poor Farm Forestry Forties). This sample was collected to represent a feedstock that may be generated following the precommercial thinnings (PCT) that often accompany natural-origin even-aged stands of loblolly pine. These small pines were delimbed, topped at approximately 5 cm diameter, and then immediately chipped using the same tractor-borne chipping attachment as used with the bolewood and slabwood. This whole-stem sample included bark, bolewood, and slabwood, and portions of what would have been classified as topwood, but no branches or foliage.

The samples from the Hope Experiment Station consisted of bolewood (HESBW01), slabwood (HESSW01), and tops and limbs (HESTL01). The Hope Experiment Station samples were comprised composite samples from three 36- to 41-cm dbh loblolly pines harvested from a stand managed using uneven-aged silviculture since 1948. The bolewood sample (HESBW01) represented sawn lumber, and the slabs generated comprised the slabwood sample (HESSW01). The "tops and limbs" sample (HESTL01) from the Hope Experiment Station consisted of the top portion of the bole (from approximately 25 cm diameter to 10 cm diameter, where the live branches were found) and the largest live pine branches (typically, these were 10-15 cm in large-end diameter). Where necessary, the topwood was also cut into smaller pieces with a portable sawmill to facilitate chipping. The topwood and limbs (no needles) from the three trees were combined to generate the final sample.

The four samples of bolewood (three replicates from Crossett and one from Hope) were taken from the interior wood of the lower bole of the sawtimber-sized trees, and were representative of "clean lumber," with the absence of any bark or outer-wood. The four samples of slabwood (three replicates from Crossett and one from Hope) were obtained by forming cants and represented the outer layers of wood and bark (if present). An example of a sawing pattern used to obtain each sample is as shown in Fig 1. Bolewood and slabwood were processed from individual trees using a portable sawmill to convert the large sawlogs into individual boards and slabs small enough (3-5 m in length, and less than 12 cm wide) to process with a modest chipper attachment connected to the power take-off shaft of a moderate-sized tractor. Chips were blown into large ag-bags in the field and then shipped to US Forest Service facilities in Pineville and Winnfield, LA, for further processing and analysis.

Feedstock Sample Preparation and Analysis

Sample preparation. All chip samples were kiln-dried to 12-13% MC and stored in labeled containers in Louisiana. Chips representing each sample were ground using a Wiley mill and subsequently classified by collecting wood meal that passed a 40-mesh sieve and were retained on a 60-mesh screen. The ground samples were air-dried and stored at room temperature and RH conditions until analysis. Chemical characterization of these samples was performed by evaluating the ultimate and proximate analyses, characteristic devolatilization temperatures, and the heating values.

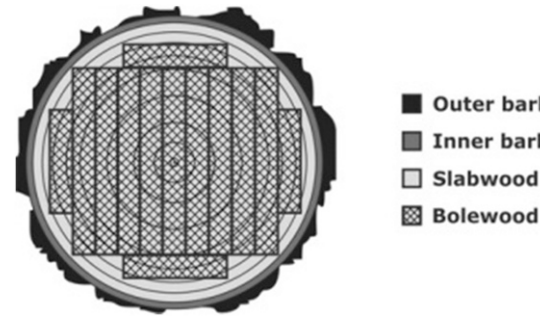

Figure 1. Schematic showing the general sawing pattern (bold lines) adopted for making cants and the selection of the slab and bole fractions of the wood.

Thermogravimetry- proximate analysis. **MC and calorimetry.** The MC of the biomass samples was determined in triplicate using an "MA 35" IR Electronic Moisture Analyzer (Sartorius AG, Göttingen, Germany). The higher heating values (HHV) were determined in triplicate using a Parr 6100 bomb calorimeter (Parr Instruments, Moline, IL), with the assumption that no sulfur was present in the pine samples.

Proximate analyses were determined in triplicate using thermogravimetry (TGA Q50 TA Instruments-Waters LLC, Lindon, UT). The samples (6-15 mg) were placed in a platinum pan, and allowed to equilibrate under nitrogen for 45 min. Next, the temperature was increased to 110°C at 20°C min^{-1} and held for 10 min to remove moisture from the sample. The sample was then heated to 550°C at 20°C min^{-1} and held for 15 min. In a final 15 min step, the sweep gas was switched from nitrogen to air to combust the char.

The proximate analysis data were determined as shown in Fig 2 as the difference between the original sample weight (point A) and those obtained at specific points along the weight–time thermogram.

MC, volatile matter, ash, and fixed carbon were calculated using the following equations (dry basis):

$$1)\ \text{Moisture Content}\,(\text{wt}\%) = \frac{(w_A - w_B)}{w_B} \times 100,$$

$$2)\ \text{Volatile Matter}\,(\text{VM})(\text{wt}\%) = \frac{(w_B - w_C)}{w_B} \times 100,$$

$$3)\ \text{Ash}\,(\text{wt}\%) = \frac{w_D}{w_B} \times 100,$$

$$4)\ \text{Fixed Carbon}\,(\text{wt}\%) = 100 - (\text{VM} + \text{Ash}).$$

This method has been utilized as an alternative to standard American Society for Testing and Materials (ASTM) procedures to determine the proximate analysis of coal (Elder 1983; Karatepe

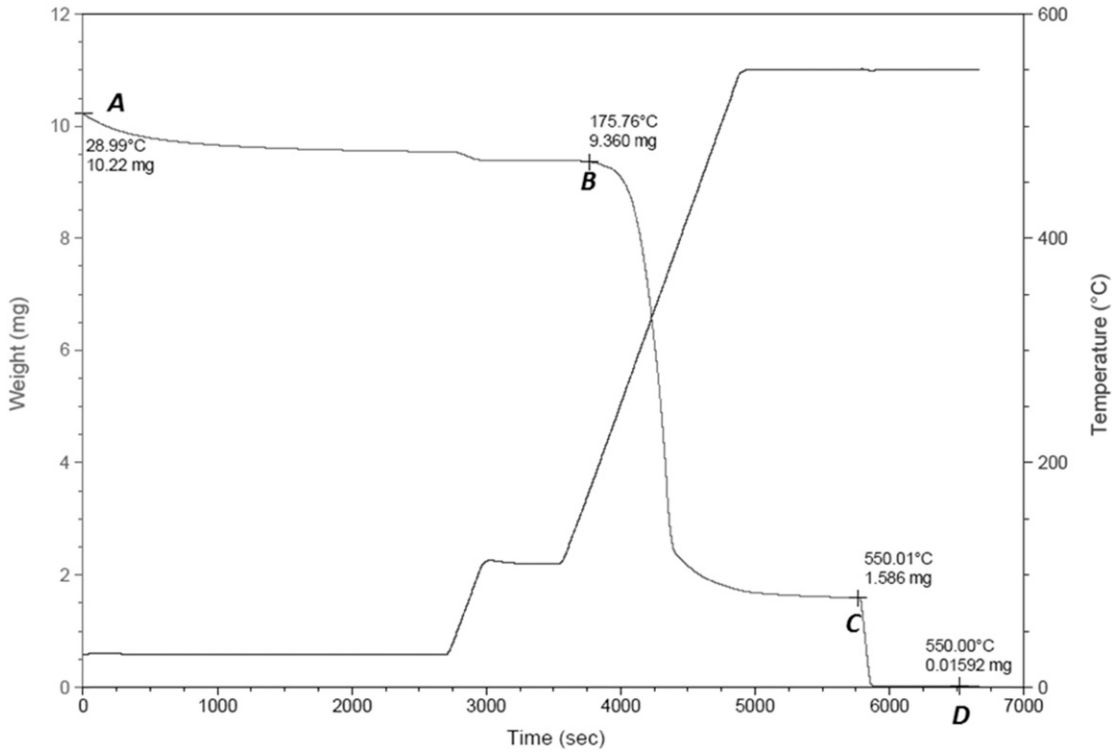

Figure 2. Methodology used for calculation of the proximate data from thermogravimetric analysis, shown for Crossett bolewood sample 3 (CEFBW03).

and Küçükbayrak 1993), biomass (Alves and Figueiredo 1988; Grønli et al 2002), plastics (Heikkinen et al 2004; Zhou et al 2006), and wastes (Heikkinen et al 2004; Skodras et al 2006), with good agreement when compared with the standard methods.

Thermogravimetry- characteristic devolatilization temperatures. Determination of the characteristic devolatilization temperatures using thermogravimetry was carried out at the same conditions that were used for performing the proximate analysis as listed previously. An approach described by Grønli et al 2002 was adopted to evaluate the characteristic temperatures that describe the devolatilization behavior of the biomass samples. An example thermogram illustrating these points is shown in Fig 3.

The residual weight percentage is plotted as a function of temperature (in °C), along with the first and second derivative curves of the weight (with respect to time). The "onset temperature," described as the point at which the devolatilization of the hemicellulose constituents begins, is determined graphically by extrapolating the slope of the $-dY/dt$ curve at the first maximum of the $-d^2Y/dt^2$ curve to zero on the ordinate. The "shoulder temperature" is identified on the curve as the value on the $-dY/dt$ curve at the first minimum of the $-d^2Y/dt^2$ curve. It corresponds with the maximum rate of hemicellulose devolatilization and is a broader region because of some overlap associated with the beginning of cellulose devolatilization. The "peak temperature," signifying the highest rate of biomass devolatilization, mostly attributable to the cellulose, is derived from the maximum of the $-dY/dt$ curve. Finally, the "offset temperature," which denotes the beginning of the tailing region attributable to lignin devolatilization, is determined by extrapolating the slope of the $-dY/dt$ curve at the second minimum of the $-d^2Y/dt^2$ curve to zero on the ordinate (Elder et al 2011).

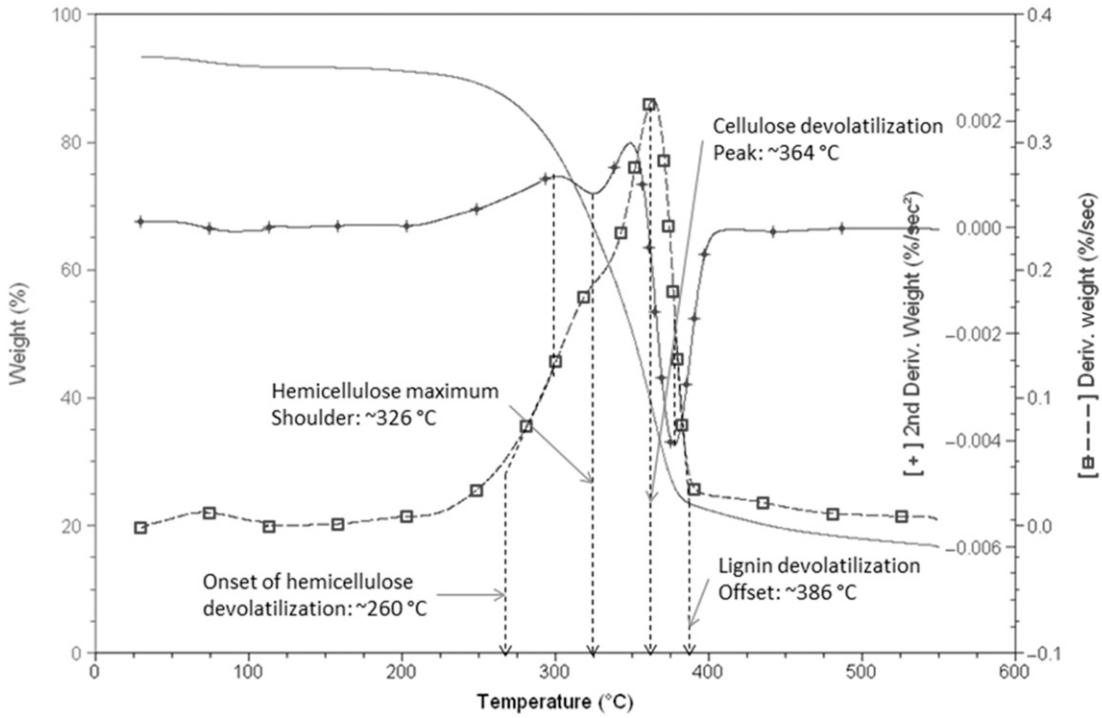

Figure 3. Example thermogram illustrating the various characteristic temperatures evaluated for each of the samples using the method of Grønli et al (2002) (shown for sample CEFBW03).

Biomass devolatilization weight loss profiles are typified by a characteristic cellulose maximum, a broad hemicellulose shoulder (because of some overlap between the cellulose and hemicellulose regions), and a baseline that pertains to a wide range of temperatures over which lignin devolatilizes (Antal and Varhegyi 1995; Grønli et al 2002). In addition, an earlier volatile emanation at lower temperatures can be attributed to the release of extracellular extractive compounds (Grønli et al 2002), which can assume importance in softwoods such as pine.

Ultimate analysis. The carbon, hydrogen, and nitrogen contents of each wood sample were measured by combustion elemental analysis using a PerkinElmer, Inc. 2400II CHNS/O combustion elemental analyzer equipped with an Autobalance AD6 microbalance (Waltham, MA). Values for carbon, hydrogen, and nitrogen contents were determined as an average of five measurements using a sample mass of approximately 5 mg; the combustion method was optimized to accommodate the larger sample size compared with the sample size normally used for the instrument (2 mg). Samples were dried at 80°C under vacuum for 48 h before weighing, then weighed and placed in tin elemental analysis cups, sealed, and stored in a desiccator until measurement.

Statistical analysis. The results were analyzed statistically using analysis of variance in SAS (SAS Institute, Inc., Cary, NC) and Tukey's test to determine the presence and nature of any differences between the samples. Significance was evaluated at the 95% probability level.

RESULTS AND DISCUSSION

Ultimate Analysis

The levels of major elements for each sample along with the results of the Tukey's test are as shown in Table 1.

The amount of carbon in all of the samples was very close to 50%, with slightly greater values observed for the whole stem and the tops and limbs samples. Collectively, the bolewood samples exhibited intermediate values of carbon, whereas the smallest amounts were observed for the slabwood samples. However, the differences between the bolewood and the slabwood samples were not statistically significant (Table 1). The oxygen content of our samples (Table 1, calculated as difference) ranged between 42.8% (for CEFWT01) and 44.1% (for CEFSW01). The whole-stem sample had the lowest oxygen content among all of the samples, which corresponds with the higher C and N content. The slightly higher carbon content in our whole stem sample might be explained by the greater contribution of bark in the material tested, which has substantially more carbon (51.1%) and less oxygen (~42%) than wood (as measured in an unspecified species of southern pine) (Mahishi and Goswami 2007).

Table 1. Amounts of C, H, and N present in the 10 samples with standard error for five observations (dry basis) rounded to two significant digits, along with the respective Tukey groups.

	C		H		N	
Sample	Average (wt%)	Tukey group	Average (wt%)	Tukey group	Average (wt%)	Tukey group
CEFSW01	49.61 ± 0.05	D	6.29 ± 0.02	A, B, C	0.04 ± 0.01	B, C
CEFSW02	49.80 ± 0.03	C, D	6.16 ± 0.04	B, C, D	0.02 ± 0.01	C
CEFSW03	49.81 ± 0.12	C, D	6.05 ± 0.03	D	0.01 ± 0.01	C
CEFBW01	50.15 ± 0.10	B, C	6.36 ± 0.05	A	0.06 ± 0.01	B, C
CEFBW02	49.98 ± 0.12	B, C, D	6.32 ± 0.03	A, B	0	C
CEFBW03	49.94 ± 0.09	B, C, D	6.21 ± 0.04	A, B, C, D	0.02 ± 0.01	C
CEFWT01	50.72 ± 0.09	A	6.21 ± 0.05	A, B, C, D	0.23 ± 0.02	A
HESBW01	50.16 ± 0.04	B, C	6.32 ± 0.01	A, B	0.10 ± 0.01	B
HESTL01	50.31 ± 0.08	B	6.23 ± 0.04	A, B, C, D	0.06 ± 0.02	B, C
HESSW01	50.08 ± 0.12	B, C	6.10 ± 0.07	C, D	0.06 ± 0.03	B, C

CEFBW, Crossett Experimental Forest bolewood; CEFSW, Crossett Experimental Forest slabwood; CEFW, Crossett Experimental Forest composite whole stem sample; HESBW, Hope Experiment Station bolewood; HESSW, Hope Experiment Station slabwood; HESTL, Crossett Experimental Forest tops and limbs.

Elementally, nitrogen and hydrogen comprised a substantially smaller fraction than carbon and oxygen. The nitrogen content of all the samples was generally very low ($\leq$0.10%, Table 1). Only the whole stem sample contained a substantial amount ($\sim$0.23%), possibly because of higher nitrogen content in the younger trees that comprised this sample—Shelton et al (1984) noted significantly higher nitrogen concentrations in younger loblolly pine. The hydrogen content for our loblolly pine samples ranged between 6.05% and 6.32% (close to the 5.97% report by Yan et al (2009)), with the bolewood samples accounting for the highest (>6.3%) amounts. Significant differences were not detected between most of the samples, although CEFBW01 and CEFSW03 contained the highest and the lowest amounts of hydrogen, respectively.

Our carbon and oxygen results are similar to those reported by Yan et al (2009), but differ slightly from those reported by others. For example, both Risser (1981) and Parikh et al (2005) found higher levels of elemental oxygen and greater carbon content in their loblolly pine forest residues. It is also interesting to note that our loblolly pine samples were very close to the customary value of 50% often assigned for the carbon content of wood. This assumption has been criticized by some as too simplistic—indeed, several reviews and other analyses have found considerable variation in carbon content as a function of tree species (Lamlom and Savidge 2003; Lamlom and Savidge 2006). For example, a study of 19 american conifers (Lamlom and Savidge 2003) showed the carbon content in the heartwood of these trees vary between 47.2% and 55.2%, with the pine species they tested varying between 50.3% and 53.3%. Nitrogen concentration varies considerably within and between trees, depending on the on-site conditions and a number of other factors; the content found in our samples (mostly between 0.04% and 0.10%) are within the reported range for loblolly pine (Shelton et al 1984; Van Lear et al 1984).

Understanding the chemistry of loblolly pine is a technically critical aspect of the viability of this feedstock in an industrial context. From the bioenergy perspective, such knowledge permits a better estimation of carbon accountability as biomass is burned and the carbon is released back into the atmosphere as greenhouse gas. This becomes more apparent during the planning and construction of large-scale biomass plants (gasifiers and combustion boilers), where a carbon balance may be necessary to describe the sustainability of individual facilities. Furthermore, determination of the elemental composition of the biomass feed can shed light on the quality of syngas produced in a commercial gasifier. Biomass elemental hydrogen can contribute toward the production of methane by reacting with carbon monoxide (methanation) during gasification, making its determination crucial toward accurate assessment of syngas quality (McKendry 2002). The hydrogen content in biomass fuels assumes significance as higher quantities can lead to the reduction of char (or of CO) to produce methane gas and water as part of the syngas product stream. High quantities of elemental oxygen render the feedstock a poorer source of fuel as it has a deleterious effect on the heating value (Huber et al 2006).

Thermogravimetric Analysis

Proximate analysis. Results of the proximate analysis for all eight feedstocks using thermogravimetry, along with the statistical interpretation using Tukey's method, are shown in Table 2.

The volatile matter content for the feedstocks ranged from 79 to $\sim$84 wt% (based on dry mass), with the whole-stem sample accounting for the lowest concentration. Differences between the Crossett bolewood and slabwood samples were not found to be significant, whereas the bolewood sample from Hope displayed significantly more volatile matter than its Crossett counterparts. Das et al (2011) reported a volatile matter content of $\sim$85% for clean pine wood chips and $\sim$84% for "tops and branches" samples, which are slightly higher than what was obtained in this study. At a constant heating rate of 20°C/min, Biagini et al (2006) reported volatile matter content for pine wood (species not specified) at

Table 2. Proximate analysis of the pine wood components as derived using thermogravimetric analysis, with standard error for triplicate analysis (dry basis) and results of the Tukey's test (samples with different letters differ significantly).

	Volatile matter		Fixed carbon		Ash content	
Sample	Average (wt%)	Tukey group	Average (wt%)	Tukey group	Average (wt%)	Tukey group
CEFSW01	82.88 ± 0.38	B, A	16.95 ± 0.35	B, D, C	0.16 ± 0.03	C
CEFSW02	82.49 ± 0.29	B, A	17.28 ± 0.27	B, D, C	0.23 ± 0.02	C
CEFSW03	82.02 ± 0.54	B, A	17.71 ± 0.51	B, A, C	0.27 ± 0.03	C, B
CEFBW01	83.83 ± 0.22	A	15.92 ± 0.21	D, C	0.25 ± 0.01	C, B
CEFBW02	84.25 ± 1.12	A	15.49 ± 1.09	D	0.26 ± 0.04	C, B
CEFBW03	83.11 ± 0.04	B, A	16.68 ± 0.09	B, D, C	0.21 ± 0.04	C
CEFWT01	79.33 ± 0.12	C	19.82 ± 0.09	A	0.85 ± 0.04	A
HESBW01	83.85 ± 0.25	A	15.87 ± 0.26	D, C	0.28 ± 0.02	C, B
HESTL01	81.48 ± 0.1	B, C	18.13 ± 0.08	B, A	0.39 ± 0.02	B
HESSW01	81.17 ± 0.42	B, C	18.55 ± 0.4	B, A	0.28 ± 0.03	C, B

CEFBW, Crossett Experimental Forest bolewood; CEFSW, Crossett Experimental Forest slabwood; CEFWT, Crossett Experimental Forest composite whole stem sample; HESBW, Hope Experiment Station bolewood; HESSW, Hope Experiment Station slabwood; HESTL, Crossett Experimental Forest tops and limbs.

83.2%, which is very close to what was observed in this study.

The fixed carbon content (the nonvolatile fraction of biomass that can be combusted to provide energy) of our samples ranged from 15.5 to 19.8 wt%, with significant differences exhibited between the whole stem (highest), "tops and limbs," followed by the rest of the samples. The Hope slabwood sample contained an amount of fixed carbon comparable with that of the whole-stem and "tops and limbs" sample. Differences were not as significant between the slabwood and the bolewood samples, and they fall in similar groups according to Tukey's test. Correlations were shown to exist between the lignin content (ash-free basis) and the fixed carbon content (Demirbaş, 2003), and as a corollary, higher values of fixed carbon in the whole stem and tops and limbs samples might be indicative of higher amounts lignin. Significant differences in ash content were exhibited between the tops and limbs, the bole and slabwood fractions, and the whole stem sample. The ash fractions contained in the "whole-stem" (0.85 wt%) and "tops and limbs" (0.39 wt%) samples were higher than that in the rest of our bolewood and slabwood (0.24 wt%) samples (Table 2). We believe that the high fraction of mineral matter in our whole-stem sample is likely attributable to the presence of bark (and possibly the addition of soil particles during the harvest process). Loblolly pine bark has a notably higher ash content than wood—Pan et al (2013) reported 1.1% in their samples. The ash content of our bolewood samples is notably lower than that of the other assessments of loblolly pine wood—eg McMillin (McMillin 1969) noted an average ash content (early and latewood) of 0.39% for young loblolly pines harvested in Louisiana.

However, unlike some work that evaluated "dirty" samples taken during conventional logging operations, the samples in this study were individually selected, felled, and then processed to minimize soil contamination. Postharvest handling of biomass also contributes to the ash content of forest residues, depending on the method of harvesting and extraction practices. Greene et al (2014) noted much higher ash contents (between 1.4 and 11.9%) for screened and unscreened roundwood and logging residues following harvesting of loblolly pine plantations in South Carolina. These high ash contents are not surprising, given that their samples included bark, needles, and considerable amounts of mineral soil (our samples contained no needles, and little to no bark or soil contamination). Even the highly organic forest floor litter contains a dramatically higher ash content than "clean" wood: Hough (1969) estimated that the ash content of the forest floor litter in Georgia loblolly pine stands ranged from 2.7% to 15.5% for the upper and lower layers, respectively.

The ash content is an intrinsic property of feedstock with considerable significance for biomass

utilization for pulp and paper, timber, and bioenergy, and this factor can be especially significant when the bioenergy applications involve combustion or gasification for the production of heat and power. Processing of feedstocks with high ash content can result in fouling, slagging, and agglomeration of the mineral matter inside biomass boilers, and can entail periodic cleanup operations to prevent corrosion. In addition, the mineral ions can either oxidize and volatilize or form particulates (Ragland et al 1991), necessitating the installation of filters to trap these evasive compounds from escaping into the environment. The mineral content of biomass is known to have a pronounced catalytic, and often unpredictable, effect on the devolatilization characteristics of biomass and has not been understood properly (Antal and Varhegyi 1995; Biagini et al 2006).

Characteristic devolatilization temperatures. The characteristic temperatures associated with devolatilization as determined by thermogravimetric analysis, and corresponding results of the Tukey's test are as shown in Table 3.

The onset of devolatilization for most of the feedstocks began at ~260°C, except for the "whole-stem" (~240°C) and the "tops and limbs" (~246°C) samples, which devolatilized at significantly lower temperatures. Bolewood samples from Crossett accounted for the highest onset temperatures, followed by the slabwood samples, whereas the corresponding samples from Hope reported significantly lower onset temperatures. Lower onset temperatures can imply a higher proportion of volatile extractives and a higher relative amount of hemicellulose in the bolewood relative to the slabwood. Biagini et al (2006) observed that the onset temperature of xylan was 253°C (making it the most reactive component apart from the extractives), which lends credence to the assumption that lower onset temperature values are also a significant function of the hemicellulose content of these samples. A higher cellulose-to-hemicellulose content would lead to slightly higher onset temperatures, although this has not been verified in this study.

The much broader shoulder temperatures, signifying the peak hemicellulose devolatilization, ranged between ~321 and ~328°C. The "whole-stem" and "tops and limbs" samples again report lower shoulder temperature values than the rest of the samples.

The peak temperatures lay between ~355 and 364°C, with the highest values obtained for the Crossett bolewood and slabwood samples. Significantly lower temperatures were needed for the maximum rate of cellulose pyrolysis in the case of the "whole-stem" and "tops and limbs" samples, along with the slabwood sample sourced from Hope.

Table 3. Average devolatilization temperatures and standard errors (for triplicate measurements) as obtained using thermogravimetry.

	Onset temperature		Shoulder temperature		Peak temperature		Offset temperature	
Sample	Average (°C)	Tukey group	Average (°C)	Tukey group	Average (°C)	Tukey group	Average (°C)	Tukey group
CEFSW01	262.11 ± 0.42	B	327.44 ± 0	A, B	363.67 ± 0	A	385.92 ± 0.19	A, B
CEFSW02	255.9 ± 0.76	D	325.74 ± 0.21	C	361.76 ± 0	B, C	385.3 ± 0.17	A, B
CEFSW03	261.54 ± 1.02	B	327.86 ± 0.21	A	363.45 ± 0.56	A	386.95 ± 0.19	A
CEFBW01	265.83 ± 0.91	A	326.16 ± 0.37	B, C	364.09 ± 0.21	A	386.24 ± 0.26	A, B
CEFBW02	263.05 ± 0.37	A, B	326.16 ± 0.37	B, C	363.67 ± 0.37	A	385.59 ± 0.94	A, B
CEFBW03	259.99 ± 0.42	B, C	325.53 ± 0	C	363.67 ± 0.37	A	385.64 ± 0.13	A, B
CEFWT01	239.57 ± 0.71	F	321.08 ± 0.63	E	355.83 ± 0.21	D	382.3 ± 0.27	C
HESBW01	258.19 ± 0.37	C, D	325.74 ± 0.21	C	363.24 ± 0.21	A, B	385.21 ± 0.27	A, B
HESTL01	246.4 ± 0.38	E	323.62 ± 0	D	360.28 ± 0.56	C	384.33 ± 0.76	B, C
HESSW01	255.43 ± 0.73	D	324.89 ± 0.37	C, D	361.35 ± 0.21	C	385.28 ± 0.04	A, B

CEFBW, Crossett Experimental Forest bolewood; CEFSW, Crossett Experimental Forest slabwood; CEFWT, Crossett Experimental Forest composite whole stem sample; HESBW, Hope Experiment Station bolewood; HESSW, Hope Experiment Station slabwood; HESTL, Crossett Experimental Forest tops and limbs.

The offset temperatures occupy a narrow window between ~382 and ~387°C, with the "whole-stem" and the "tops and limbs" samples accounting for the lowest temperatures. Differences between the rest of the samples are not significant, as indicated by the results of the Tukey test.

Biagini et al (2006) reported similar values for the characteristic devolatilization temperatures of pine wood, with thermogravimetry conducted at a constant heating rate of 20°C/min.

Calorimetry

The average HHV, along with the standard errors for triplicate measurements and statistical differences between individual samples obtained using the Tukey's test are shown in Table 4.

Samples CEFSW03, CEFBW02, and CEFWT01 have the highest HHV values at more than 18.5 MJ/kg. These values are substantially lower than the HHV reported by White (1987) for southern pine (20.68 MJ/kg) and the range (20-22.24 MJ/kg) for softwoods reported by Ragland et al 1991. Yan et al (2009) provided a slightly higher HHV of ~19.54 MJ/kg for dried loblolly pine chips, but this could be attributed to their estimation of the HHV on a bone-dry basis.

In general, a higher content of lignin is responsible for greater values of the HHV in biomass, as the HHV of lignin (23.26-25.59 MJ/kg) is substantially higher than that of holocellulose (~18.61 MJ/kg) (Demirbaş, 2001). In comparison with dedicated energy crops, the energy content values obtained in this study are comparable with that of switchgrass (~18.61 MJ/kg) and slightly lower than that of poplar (~19.77 MJ/kg) (McLaughlin et al 2002), suggesting loblolly pine as an acceptable source for bioenergy considering its much lower ash content (vs 7.1 wt% for switchgrass and 1.3 wt% for poplar) (Esteghlalian et al 1997), which makes it a favorable feedstock for gasification applications.

Table 4. Average HHV (MJ/kg) and standard errors (for triplicate measurements) and results of the Tukey's test.

Sample	Tukey group	Mean HHV (MJ/kg)
CEFSW03	A	18.82 ± 0.21
CEFBW02	B, A	18.70 ± 0.06
CEFWT01	B, A	18.70 ± 0.06
CEFBW01	B, A, C	18.38 ± 0.05
HESBW01	B, C	18.33 ± 0.09
HESSW01	B, D, C	18.25 ± 0.04
CEFSW01	D, C	18.00 ± 0.05
CEFBW03	E, D	17.79 ± 0.04
CEFSW02	E	17.53 ± 0.13
HESTL01	F	16.8 ± 0.06

CEFBW, Crossett Experimental Forest bolewood; CEFSW, Crossett Experimental Forest slabwood; CEFWT, Crossett Experimental Forest composite whole stem sample; HESBW, Hope Experiment Station bolewood; HESSW, Hope Experiment Station slabwood; HESTL, Crossett Experimental Forest tops and limbs; HHV, higher heating values.

Bioenergy Implications of Natural-Origin Loblolly Pine

Our samples from natural-origin loblolly pine are well within the range of previously published chemistry values for this species, suggesting that this material is adequately suited for bioenergy feedstocks. If properly developed, logging slash, underutilized mill residues, and mill waste products represent an opportunity to improve provisional ecosystem services from naturally regenerated pine-dominated stands while posing few, if any, impacts on traditional lumber, panel, and paper production (Parikka 2004; Perlack and Stokes 2011). Topwood, eg, is generally considered an inferior feedstock for making paper because of higher pulping costs resulting from its higher lignin content (Pearson et al 1980). Currently, most of this material is either left in the woods to decompose, is piled and burned as a part of the site preparation practices, or is chipped and used as a low-value "hog fuel" to generate heat, steam, and/or electricity. Better utilization of these residues provides new opportunities for existing industries: Frederick et al (2008) promoted the more efficient use of the loblolly pine wood in a kraft pulping facility to produce conventional outputs (cellulose for paper), as well as ethanol (via hydrolysis), and heat/steam and electrical power using other residues from the pulping process.

Increasing the quantity of wood produced from the forest by utilizing this form of biomass can

simultaneously achieve other forest management objectives such as improving tree growth, quality, and stand health. For example, the PCT of dense, naturally regenerated southern pine stands to promote rapid growth, shorten rotation length, and improve forest health has been promoted for years (Grano 1969; Mann and Lohrey 1974; Cain 1996; Nowak et al 2008). However, some landowners have considered PCT as problematic because this competition control measure is (by definition) an up-front cost which may not be recouped until many years later. The expense of PCT has led some landowners to avoid this practice; however, if small young pines can be commercially utilized for bioenergy, better silvicultural outcomes can be encouraged. Other opportunities to improve upon silvicultural practices based on bioenergy opportunities have been noted, particularly those that help mitigate wildfire risk (Polagye et al 2007) or significantly reduce site preparation costs, particularly for loblolly pine plantations (Gan and Smith 2007).

However, the results of this study did find some modest chemistry-related differences between samples of young and older pines (eg nitrogen content) or wood only vs whole tree (eg ash content), which have large-scale implications for forest health and productivity. McMillin (1969) speculated that the differences he witnessed in ash content of loblolly pine wood, when coupled with the proportion of earlywood and growth rate, would translate into meaningful stand-level outcomes between planted and natural-origin stands. For example, harvesting large quantities of high nutrient concentration young loblolly pines grown in short-rotation bioenergy plantations could deplete some sites of nutrients faster than they can be replaced, requiring additional inputs (eg fertilizers) to retain productivity (Eisenbies et al 2009). A similar issue could arise in the utilization of logging residues, as the branches, foliage, and bark of harvested loblolly pine contain a disproportionate amount of nutrients and soil organic matter compared with their biomass yield, and hence, their increased utilization could result in a long-term tradeoff with decreased site productivity, lessened water quality, and diminished wildlife habitat (Scott and Dean 2006; Eisenbies et al 2009; Perlack and Stokes 2011). Further work is required to ensure that overall ecosystem service provisioning is not adversely affected by increased bioenergy-related production in natural-origin loblolly pine stands.

CONCLUSIONS

The chemical characterization performed in this study reaffirms the advantages of utilizing loblolly pine as a bioenergy feedstock. Acceptable energy content and relatively low ash content in the natural-origin loblolly pine samples tested suggest that this feedstock is well-suited for combustion and gasification. Subtle differences were observed within most of the chemical properties of the individual wood fractions, with significant variations discovered for the "whole-stem" and "tops and limbs" samples. The differences among the latter samples were most likely due to the type of wood present (compression wood and branchwood). Despite sourcing samples from two different stands in southern Arkansas, no significant differences could be witnessed as a result of biomass origin, suggesting that the dependence of chemical properties was based more on the wood fraction.

Dedication of the forest floor residue (tops and branches) for bioenergy purposes could be a viable option, considering it is an inexpensive and fairly ubiquitous feedstock. Similar arguments may be made for promoting the use of whole-stem samples, given their relatively high energy content (among the highest for the samples analyzed in this study) and an ash content that is acceptable for gasifier applications. The applicability of these two fractions may be hindered by the nonhomogeneous nature of the feed in terms of particle size and shape and lower bulk density, which can lead to issues in handling and feeding into gasifiers. Large-scale use of tops, limbs, and branches will require investigations into better handling techniques for pilot and commercial-scale gasifiers if the advantages of using these fractions are to be fully realized. Feedstock that is fine-grained, "fluffier," and of low bulk densities

has been documented to adversely affect flow through the bunker section of the gasifier along with large pressure drops in the reduction zone, which consequently lead to lower temperatures and tar production, especially in downdraft systems (FAO 1986).

This article also shows that underutilized biomass feedstocks from natural-origin loblolly pine, if properly developed, could yield considerable biofuel-related value-added opportunities for foresters and landowners in the southeastern United States. Although pine plantations currently comprise nearly one-fifth of the 830,000 km^2 of forestland in this region (Wear and Gries 2012), naturally regenerated pine-dominated forests still cover approximately one-sixth of the area. Biomass for bioenergy represents another provisional ecosystem service that, when properly applied, should be compatible with the multifunctional management of naturally regenerated, southern pine–dominated stands, and is an attractive alternative to potentially invasive feedstocks (Quinn et al 2014). However, further study is still needed to ensure that increased utilization of residues does not come at the expense of other critical ecosystem services.

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