# ASSESSMENT OF APPALACHIAN HARDWOOD RESIDUE PROPERTIES AND POTENTIALS FOR BIOENERGY UTILIZATION

Adebola Adebayo†

Graduate Research Assistant

Jingxin Wang\*†

Associate Professor

## Benjamin Dawson-Andoh<sup>†</sup>

Associate Professor

## Joseph F. McNeel

Professor and Director

## James P. Armstrong<sup>†</sup>

Associate Professor West Virginia University Division of Forestry and Natural Resources Morgantown, WV 26506

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Abstract. Logging residue specimens of yellow-poplar and red oak were collected from 15 previously harvested sites across West Virginia. Sites were selected with respect to the varying soil compositions based on a USDA soil survey as well as to the average annual precipitation regions. Wood specimens were then analyzed for their physical, chemical, and thermal properties. Results indicated that logging residues of yellow-poplar and red oak were dried in nature to 7.4 - 39% MC. Yellow-poplar sapwood-specific gravity reduced by 15 and 26.5% on average after 2 and 3 yr of ground contact, respectively. Red oak sapwood-specific gravity was lower than its heartwood by 26.6, 25.3, and 8.2% for the 2005, 2006, and 2007 harvest years, respectively. Chemical analysis showed higher extractives and lignin contents for decayed wood samples collected in 2005 harvested sites. Heating value showed no significant difference between sapwood and heartwood residues of undecayed and decayed material. Our analysis on the potential sugars available showed that about 85 - 90% of 1.02 billion kg of sugars derivable from wood residues in West Virginia could be fermented to ethanol or butanol.

Keywords: Logging residue; properties; decay; proximate; heating value; bioenergy.

#### INTRODUCTION

The current price of crude oil is significantly greater than 10 yr ago. Statistics show that the price of fuels and petrochemical products may continue to increase indefinitely in the United States as a result of overdependence on dwindling nonrenewable petroleum resources. This overdependence has consistently been increasing according to the Energy Information Administration statistics (USDOE 2005). For example, net petroleum product imports increased 16.8% in January 2005, crude oil net imports increased 5.3%, and natural gas net imports increased 3.8%.

One promising solution to these challenges is the use of waste biorenewable resources such as woody biomass to produce energy. There exist abundant wood residues in the US that could be converted into fuels (Perlack et al 2005). For example, West Virginia produces an

<sup>\*</sup> Corresponding author: jxwang@wvu.edu

<sup>†</sup> SWST member

estimated 2.41 billion kg of dry wood residues per year, including 1.34 billion kg logging residue of which red oak is the predominant species group by weight, averaging  $1.3 \text{ kg/m}^2$ , followed by yellow-poplar and maple species with 0.3 kg/m<sup>2</sup> (Grushecky et al 2006; Wang et al 2006).

There is a growing demand for more efficient utilization of biomass residue through direct combustion, gasification, and fermentation technologies to complement the use of nonrenewable coal resources in the Appalachian region. This is of particular interest because wood is renewable and environmentally friendly compared with coal.

One problem with using logging wastes is decay. Previous studies indicate that weathering and decay resulting from extended exposure in the environment affect the physical, chemical, and anatomical properties of wood (Anderson et al 1990; Wilhelmsson 2006). However, the magnitude of the effects of environmental exposure of Appalachian hardwoods is poorly understood with no specific documentation for logging residues. This study addresses the need for better understanding of the effects of environmental exposure on the physical, chemical, and heatrelated properties of logging residues of the two most abundant Appalachian hardwood species and their potential for bioenergy production.

#### MATERIALS AND METHODS

#### **Materials**

During the summer of 2007, log residues were collected based on a  $5 \times 3 \times 2 \times 2$  factorial experiment in a completely randomized design with 10 replicates. In this design, the four main factors considered were forest district locations (five), years of harvest (2005, 2006, and 2007), species [red oak (*Querus rubra*) and yellow-poplar (*Liriodendron tulipifera*)], and position of the specimens within the diameter (sapwood or heartwood). Logging residues were collected from previously harvested sites within the five locations. Throughout the state, collection areas were selected from the major soil types based on a USDA soil survey and average annual

precipitation. Within each distinct location, three harvested sites were randomly selected from a list of all harvests in 2005, 2006, and 2007 using the West Virginia Division of Forestry logging notification forms. Notification of timber harvesting in West Virginia is mandated under the 1992 Logging Sediment Control Act (WVDOF 2005) under which all loggers are required to submit a harvest plan within 3 da of starting a new timbering operation. At each collection area, three discs (102 mm thick) of large-end diameters of 203 – 253 mm were collected for red oak and yellow-poplar. This diameter range was based on a survey conducted in 2002 (Grushecky et al 2006).

#### Methods

After the residues were collected from the designated sites, each specimen was processed into blocks of  $10 \times 10 \times 40$  mm for MC and specific gravity determination using a gravimetric method.

Lignin, extractives, and holocellulose in the wood were determined in accordance with ASTM D 1110-84; 1106-96 (ASTM 2001). Proximate analysis, ie content of volatile matter, carbon, and ash in wood, was determined according to ASTM D3172 (ASTM 2006) and D1102-84 (ASTM 2001). All pulverized samples used for heat value determination were oven-dried to 0% MC. One gram of each sample was placed in an oxygen bomb calorimeter (Parr 6300) for heat determination. After running each sample through the bomb calorimeter, corrections were made based on the calorimeter gross and net heat of combustion (Eqs 1 and 2) and combustion (Eq 3) for hydrogen, nitric acid, and sulfuric acid, and fuse wire consumption for the final computation of the gross and net heating value of each wood specimen following ASTM E711-87 (ASTM 2006). At the completion of all physical, chemical, proximate, and thermal tests on the logging residues, analysis of variance with a Duncan multiple comparison test was performed using SPSS statistical software (SPSS Inc., Chicago, IL).

$$H_c = (WT - e_1 - e_2 - e_3)/kg$$
 (1)

$$\begin{bmatrix} C_a H_b O_c N_d S_e + (4a+b+\frac{d}{2}+e-2c) O_2 \\ \rightarrow a C O_2 + \left(\frac{b}{2}\right) H_2 O + \left(\frac{d}{2}\right) N O_2 + e S O_2 \tag{2}$$

$$H_n = 1.8H_c - 92.7H$$

$$C_{a}H_{b}O_{c}N_{d}S_{e} + (4a+b+\frac{d}{2}+e-2c)O_{2}$$
  

$$\rightarrow aCO_{2} + {\binom{b}{2}}H_{2}O + {\binom{d}{2}}NO_{2} + eSO_{2}$$
(3)

where:

- $H_c = gross heat combustion (J/kg)$
- T = observed temperature rise ( $^{\circ}$ C)
- W = energy equivalent of calorimeter used (J/kg)
- $e_1$  = heat produced by burning nitrogen in air (J)
- e<sub>2</sub> = heat produced by formation of sulfuric acid in bomb (J)
- $e_3$  = heat produced by heating wire and tread (J)
- m = mass of sample (kg)
- $H_n = net heating value (J/kg)$
- H = hydrogen (%)

#### **RESULTS AND DISCUSSION**

#### **Physical Properties**

The measured physical properties (specific gravity and MC) of yellow-poplar and red oak logging residues from the 2005 - 2007 harvests are given in Tables 1 and 2. MC in the logging residue samples was significantly different (P < 0.0001) among district locations, harvest year, species, heartwood, and sapwood. MC differences were relatively low between year of harvest and species with minimal variation between heartwood and sapwood within each district. 2007 - 2006 residues had significantly higher MCs than 2005 residues (P < 0.0001); MC of heartwood was significantly higher than sapwood (P < 0.0001). Generally, the results indicate that logging residues of yellow-poplar and red oak have been air-dried in the environment to an MC range of 7.4 - 39% resulting from cyclical exposure to humidity and temperature over an extended period of time. The only exception to the low moisture trend observed was in red oak residues with 72% sapwood MC. This high MC was a result of increased precipitation before the wood residue collection. Although all the logging residues across the state were naturally dried to about the same MC, the hygroscopic nature of wood drives it to absorb moisture until it reaches equilibrium with the prevailing environmental conditions. The moisture range of 7.4 - 39% observed in this study is lower than the green wood MC range of 80 - 100% and is advantageous for transportation cost, processing, drying, and wood combustion.

A significant (P < 0.0001) decreasing trend in sapwood-specific gravity was demonstrated with increased exposure on-site (Fig 1) as previously reported for various hardwood species (Smith et al 2007). Differences between sapand heartwood-specific gravity wood of yellow-poplar and red oak residues (Tables 1 and 2) were significant (P < 0.0001). There was an approximately 3% difference between heartwood and sapwood-specific gravities of yellow-poplar wood in the 2007 harvest year, whereas 2006 and 2005 harvest samples showed significant (P < 0.0001) reductions in sapwoodspecific gravity values as compared with heartwood. Yellow-poplar sapwood-specific gravity was reduced by an average of 15% after 2 yr (2006) and 26.5% after 3 yr (2005) of ground contact when compared with heartwood samples. Similarly, the specific gravities for samples of red oak sapwood were lower than heartwood by 26.6, 25.3, and 8.2% for 2005, 2006, and 2007 harvest years, respectively. The reason for the higher reduction of specific gravity in 2006 - 2005 samples could be attributed to greater sapwood decay from extended exposure to favorable environmental conditions for growth and development of biodeterioration agents and weathering (Highley 1995; FPL 1999).

Decay as evaluated by environmental exposure time, visual observation of significant color changes, and weight loss on wood from inside

| Year of harvest   | Forest district |              |              |              |             |  |
|-------------------|-----------------|--------------|--------------|--------------|-------------|--|
|                   | 1               | 3            | 4            | 5            | 5           |  |
| 2005              |                 |              |              |              |             |  |
| Dia. (mm)         | 203.0           | 216.0        | 229.0        | 178.0        | 191.0       |  |
| Percent decay     | 50              | 36           | 53           | 100          | 53          |  |
| Sap SG            | 0.28 (0.05)     | 0.31 (0.13)  | 0.43 (0.05)  | 0.34 (0.05)  | 0.38 (0.05) |  |
| Sap MC            | 10.76 (0.73)    | 16.6 (1.33)  | 11.60 (1.31) | 39.33 (8.79) | 7.45 (1.10) |  |
| Heart SG          | 0.48 (0.07)     | 0.56 (0.05)  | 0.45 (0.06)  | 0.43 (0.08)  | 0.48 (0.06) |  |
| Heart MC          | 10.57 (0.34)    | 24.48 (1.85) | 12.56 (0.86) | 33.47 (6.8)  | 8.0 (0.81)  |  |
| 2006              |                 |              |              |              |             |  |
| Dia. (mm)         | 229.0           | 203.0        | 241.0        | 178.0        | 178.0       |  |
| Percent sap/decay | 40              | 35           | 42           | 76           | 46          |  |
| Sap SG            | 0.42 (0.038)    | 0.45 (0.09)  | 0.49 (0.04)  | 0.42 (0.05)  | 0.56 (0.03) |  |
| Sap MC            | 18.80 (1.20)    | 21.23 (6.87) | 9.25 (1.63)  | 10.85 (1.38) | 8.40 (0.43) |  |
| Heart SG          | 0.49 (0.03)     | 0.56 (0.05)  | 0.47 (0.10)  | 0.45 (0.04)  | 0.67 (0.06) |  |
| Heart MC          | 25.09 (3.78)    | 25.77 (1.93) | 10.84 (0.71) | 11.97 (1.33) | 8.40 (0.67) |  |
| 2007              |                 |              |              |              |             |  |
| Dia. (mm)         | 229.0           | 229.0        | 254.0        | 203.0        | 254.0       |  |
| Percent sap       | 55              | 35           | 50           | 50           | 40          |  |
| Sap SG            | 0.49 (0.05)     | 0.44 (0.03)  | 0.46 (0.20)  | 0.44 (0.02)  | 0.49 (0.04) |  |
| Sap MC            | 17.09 (2.5)     | 25.05 (1.22) | 15.78 (7.37) | 7.41 (0.42)  | 7.75 (0.30) |  |
| Heart SG          | 0.48 (0.03)     | 0.49 (0.07)  | 0.51 (0.13)  | 0.41 (0.02)  | 0.43 (0.06) |  |
| Heart MC          | 16.49 (2.5)     | 26.17 (7.69) | 14.37 (5.53) | 7.18 (2.00)  | 7.35 (0.86) |  |

Table 1. Specific gravity (SG) and percentage MC of yellow-poplar by district and year of harvest.

SD shown in parentheses.

| Table 2  | Specific gravity (SG) and percentage MC of red oak by district and year of harvest.   |
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|                   | Forest district |              |              |              |             |  |
|-------------------|-----------------|--------------|--------------|--------------|-------------|--|
| Year of harvest   | 1               | 3            | 4            | 5            | 5           |  |
| 2005              |                 |              |              |              |             |  |
| Dia. (mm)         | 229.0           | 229.0        | 254.0        | 229.0        | 191.0       |  |
| Percent decay     | 32              | 17           | 10           | 44           | 53          |  |
| Sap SG            | 0.49 (0.09)     | 0.43 (0.06)  | 0.48 (0.08)  | 0.55 (0.07)  | 0.39 (0.05) |  |
| Sap MC            | 11.66 (4.86)    | 10.16 (0.82) | 12.44 (1.30) | 72.11 (11.0) | 7.45 (1.10) |  |
| Heart SG          | 0.66 (0.04)     | 0.72 (0.14)  | 0.73 (0.10)  | 0.64 (0.05)  | 0.48 (0.06) |  |
| Heart MC          | 20.78 (3.14)    | 13.18 (0.97) | 18.44 (1.94) | 28.28 (3.08) | 8.06 (0.85) |  |
| 2006              |                 |              |              |              |             |  |
| Dia. (mm)         | 229.0           | 229.0        | 254.0        | 203.0        | 178.0       |  |
| Percent sap/decay | 10              | 17           | 15           | 25           | 23          |  |
| Sap SG            | 0.54 (0.03)     | 0.47 (0.09)  | 0.58 (0.07)  | 0.52 (0.08)  | 0.57 (0.03) |  |
| Sap MC            | 11.75 (0.66)    | 9.60 (0.51)  | 14.00 (1.67) | 15.39 (3.03) | 8.40 (0.43) |  |
| Heart SG          | 0.62 (0.03)     | 0.72 (0.04)  | 0.74 (0.08)  | 0.90 (0.05)  | 0.67 (0.06) |  |
| Heart MC          | 16.85 (1.16)    | 9.40 (0.92)  | 15.84 (5.03) | 38.08 (5.59) | 8.40 (0.67) |  |
| 2007              |                 |              |              |              |             |  |
| Dia. (mm)         | 241.0           | 241.0        | 254          | 229.0        | 254.0       |  |
| Percent sap       | 10              | 17           | 10           | 9            | 20          |  |
| Sap SG            | 0.61 (0.10)     | 0.70 (0.14)  | 0.60 (0.05)  | 0.52 (0.03)  | 0.49 (0.05) |  |
| Sap MC            | 18.84 (2.98)    | 12.54 (0.64) | 14.06 (1.41) | 7.76 (0.52)  | 7.7 6(0.31) |  |
| Heart SG          | 0.70 (0.07)     | 0.74 (0.05)  | 0.62 (0.01)  | 0.56 (0.04)  | 0.43 (0.06) |  |
| Heart MC          | 27.57 (2.22)    | 13.97 (0.66) | 17.36 (1.02) | 8.46 (0.94)  | 7.52 (0.07) |  |

SD shown in parentheses.

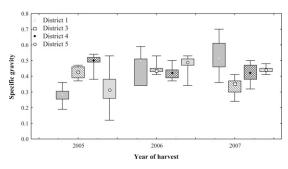


Figure 1. Yellow-poplar (sapwood)-specific gravity variability among districts and year of harvest.

bark to pith ranged from 36 - 100% for the 2005 harvest and 35 - 76% for the 2006 harvest for yellow-poplar residues. Lower decay of 10 -25% was observed for red oak residues (Tables 1 and 2). Based on the observed decay, heartwood samples of yellow-poplar and red oak were found to be more resistant to decay than their sapwood counterparts. It has been previously reported that the heartwood of some tree species such as oak, Douglas fir, and certain pines are more resistant to decay as a result of their phenol, terpene, alkaloid, and toxic extractives (Scheffer and Cowling 1966). Wood also decays faster in the humid and warm environment of the Appalachian hardwood forests as a result of the mechanical breakdown by insects and borers and biochemical breakdown by white-, brown-, and soft-rot fungi (Scheffer and Cowling 1966).

### **Chemical Properties**

Measured chemical properties (extractives, lignin, and holocellulose) content of yellow-poplar and red oak residues (Tables 3 and 4) generally agreed with that obtained in a previous study (White 1987). Differences in extractive contents were highly significant (P < 0.0001) between heartwood and sapwood across year of harvest, district location, and wood species. The extractives of 2005 residues were about 20% more than the extractives of undecayed wood residues in the 2006 and 2007 harvest years. Figure 2 shows an exceptionally high extractive content (17%) for 2005 yellow-poplar residues. Lower holocellulose content was found in decayed sapwood samples of yellow-poplar and red oak residues than in fresh residues from the 2007 harvest at the expense of proportionately higher extractives and lignin contents. The lower holocellulose content observed on decayed wood (Fig 3) was a result of microbial-mediated biochemical changes as previously reported (Rowell 1984; Pandey and Nagveni 2007). During fungi growth on wood, cellulose and hemicellulose are the desired carbon sources for the energy required for growth and development. Holocellulose is biochemically broken down into six-carbon sugars for enzymatic hydrolysis, leading to reduced holocellulose content in decayed wood residues. This also explains the higher sapwood extractive contents of decayed vellow-poplar and red oak wood samples because remnants of decomposed holocellulose and weathered lignin content leached out together with the remaining extractives during wood solubility tests.

The observed holocellulose content (from 60 – 73%) is representative of the potential amount of sugars (5- and 6-carbon) that could be converted through a host of fermentation processes into ethanol, butanol, and other liquid fuels. In addition, extracted lignin can also be efficiently used as an emulsifier in animal feed, raw material in the production of vanillin, in pharmaceuticals, as a fragrance in perfume products, and a binder in ceramic and wood composite industries (Northey 1992).

Assuming that 60% of all the annual dry wood residues of 2.41 billion kg in West Virginia can be economically accessed, this residue would potentially support about five ethanol plants (processing 725,600 kg/da) or other biofuel plants based on a feasibility study by the Quincy Library Group (QLG 1997). On the basis of our chemical analysis, about 1.02 billion kg of sugars, 0.36 billion kg of lignin, and 0.06 billion kg of extractives could be generated from the 60% of the annually generated logging waste.

Based on a biomass-to-ethanol feasibility study in California, approximately 85 – 90% of

|                         | Year of harvest |              |              |  |
|-------------------------|-----------------|--------------|--------------|--|
| Properties              | 2005            | 2006         | 2007         |  |
| Percent sap-decay range | 53 - 100        | 40 - 70      | 40 - 50      |  |
| Sapwood chemical (%)    |                 |              |              |  |
| Extractives             | 11.00 (3.26)    | 8.29 (1.62)  | 8.00 (1.14)  |  |
| Holocellulose           | 67.94 (7.31)    | 73.08 (4.93) | 72.67 (2.3)  |  |
| Lignin                  | 32.06 (7.31)    | 25.25 (3.70) | 27.33 (2.3)  |  |
| Proximate analysis (%)  |                 |              |              |  |
| Volatile                | 80.90 (2.71)    | 80.77 (1.03) | 82.5 (3.77)  |  |
| Fixed carbon            | 19.1 (2.71)     | 19.23 (1.03) | 17.5 (3.77)  |  |
| Ash                     | 0.62 (0.2)      | 0.62 (0.24)  | 0.64 (0.26)  |  |
| Heat value (kJ)         |                 |              |              |  |
| Net                     | 7.99 (0.54)     | 7.71 (0.26)  | 7.74 (0.40)  |  |
| Gross                   | 8.54 (0.54)     | 8.26 (0.26)  | 8.27 (0.40)  |  |
| Heartwood chemical (%)  |                 |              |              |  |
| Extractives             | 8.30 (1.46)     | 8.30 (1.16)  | 9.28 (2.4)   |  |
| Holocellulose           | 71.18 (6.41)    | 72.1 (3.34)  | 71.71 (6.4)  |  |
| Lignin                  | 27.65 (5.95)    | 27.92 (3.34) | 28.29 (6.4)  |  |
| Proximate analysis (%)  |                 |              |              |  |
| Volatile                | 80.27 (1.70)    | 81.23 (1.27) | 80.82 (1.07) |  |
| Fixed carbon            | 19.73 (1.70)    | 18.77 (1.27) | 19.18 (1.07) |  |
| Ash                     | 0.67 (0.34)     | 0.59 (0.32)  | 0.62 (0.24)  |  |
| Heat value (kJ)         |                 |              |              |  |
| Net                     | 7.85 (0.27)     | 7.65 (0.21)  | 7.72 (0.15)  |  |
| Gross                   | 8.39 (0.27)     | 8.19 (0.21)  | 8.27 (0.15)  |  |

Table 3. Chemical and heat related properties of yellow-poplar by year of harvest.

SD shown in parentheses.

 Table 4. Chemical and heat-related properties of red oak wood by year of harvest.

| Properties              | 2005        | 2006        | 2007        |
|-------------------------|-------------|-------------|-------------|
| Percent sap-decay range | 10 - 53     | 10 - 46     | 10 - 40     |
| Sapwood chemical (%)    |             |             |             |
| Extractives             | 11.3 (3.1)  | 11.5 (3.1)  | 8.5 (1.7)   |
| Holocellulose           | 58.7 (6.8)  | 60.7 (3.3)  | 70.4 (4.2)  |
| Lignin                  | 41.4 (6.8)  | 39.3 (3.3)  | 29.6 (4.2)  |
| Proximate analysis (%)  |             |             |             |
| Volatile                | 79.2 (7.8)  | 79.6 (1.2)  | 79.5 (1.0)  |
| Fixed carbon            | 21.3 (7.9)  | 20.7 (1.1)  | 20.7 (1.1)  |
| Ash                     | 0.58 (0.28) | 0.84 (0.16) | 0.34 (0.07) |
| Heat value (kJ)         |             |             |             |
| Net                     | 8.10 (0.39) | 7.82 (0.20) | 7.79 (0.16) |
| Gross                   | 8.65 (0.39) | 8.37 (0.20) | 8.34 (0.16) |
| Heartwood chemical (%)  |             |             |             |
| Extractives             | 12.4 (4.0)  | 11.6 (1.4)  | 9.9 (1.2)   |
| Holocellulose           | 67.4 (8.5)  | 60.1 (4.9)  | 68.2 (5.9)  |
| Lignin                  | 32.6 (8.5)  | 39.9 (4.9)  | 31.8 (5.9)  |
| Proximate analysis (%)  |             |             |             |
| Volatile                | 81.5 (7.2)  | 78.5 (1.1)  | 79.0 (1.0)  |
| Fixed carbon            | 19.1 (7.4)  | 21.8 (1.2)  | 27.5 (1.0)  |
| Ash                     | 0.58 (0.28) | 0.66 (0.82) | 0.23 (0.09) |
| Heat value (kJ)         |             |             | . ,         |
| Net                     | 7.88 (0.25) | 7.61 (0.25) | 7.81 (0.22) |
| Gross                   | 8.42 (0.25) | 8.15 (0.25) | 8.35 (0.22) |

SD shown in parentheses.

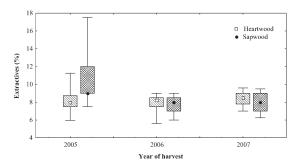


Figure 2. Variability of yellow-poplar extractive content from five districts by year of harvest (2005, 2006, 2007) and location in sapwood (sap) and heartwood (heart) of tree bole.

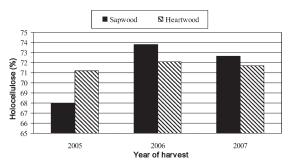


Figure 3. Variability of yellow-poplar holocellulose content across the districts by year of harvest and location in wood (sapwood vs heartwood).

1.02 billion kg of 6-carbon sugars (glucose, mannose, and galactose) derived from wood can be fermented to ethanol at bench scale using *Saccharomyces cerevisiae* (Kadam et al 2000). The results obtained on specific gravity (SG), effect of environmental exposure (E) or decay factor, and exposure length (T) was used to develop a predictive (Eq 4) for the future analysis of biomass-to-ethanol production in West Virginia.

SG = 
$$0.72 - 0.20E + 0.002T$$
 ( $r^2 = 0.48$ , RMSE  
=  $0.071$ ,  $P = 0.0001$ ) (4)

where:

T = 0, 24, and 36... for yr 1, 2, and 3

A 10-yr simulation using Eq 4 to predict yellow-poplar wood loss resulting from effect

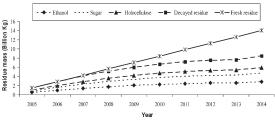


Figure 4. Ten years of simulation for potential residue accumulation and conversion to ethanol.

of environmental exposure indicated an increase in biomass accumulation at a decreasing rate leading to over 50% reduction in total logging residue when compared with fresh residues (ie assuming no wood decay) in West Virginia (Fig 4). Although a significant amount of logging residue would be lost to decay, enough biomass still exists (about 1.5 billion kg/yr) for sugar production to support potential ethanol plants. However, there would be a need for two other plants to consume wastes (about 83% loss of the original solid wood residues before final conversion to ethanol) generated from extractives, lignin, and solid substrates from fermentation.

# Proximate Analysis and Higher Heating Value

Volatiles, fixed carbon, and ash content of decayed and undecayed wood residue samples were less variable with year of harvest and between heartwood and sapwood of yellow-poplar and red oak (Tables 3 and 4). Volatile matter averaged about 80%, fixed carbon around 20%, and ash content about 1% (Tables 3 and 4). These were in agreement with values reported previously (Sjöström 1981; Demirbas 1997). The only exception to this general trend was in 2007 red oak heartwood residue with a fixed carbon content of 27.5%. Although red oak had more wood elements per unit volume than yellow-poplar, and more material in undecayed wood than decayed (Tables 1 and 2), there were no observable significant differences in the volatile content resulting from the particulate nature of the samples used for the proximate analysis. These woods yielded about the same

proximate content, but in reality, a less dense wood like yellow-poplar or decayed yellowpoplar wood would contain more wood material in proportion to its specific gravity to provide an equivalent proximate content of undecayed wood. For example, decayed yellow-poplar wood of specific gravity 0.23 is 50% less dense than an undecayed wood sample. Equal volumes of the decayed vs undecayed wood when processed into dust will result in the decayed sample having 50% less wood dust compared with an undecayed vellow-poplar sample. As a result of this constraint, a carbonization experiment at temperature range of  $150 - 750^{\circ}$ C was carried out using uniform-sized blocks vs wood dust for undecayed (2007 harvest) and decayed (2005 harvest) vellow-poplar residue. At a range of 300 - $600^{\circ}$ C, results showed significant differences (P < 0.0001) between decayed and undecayed wood blocks and wood dust residues with each sample corresponding inversely to specific gravity of wood, ie less dense decayed yellow-poplar residue had the highest volatile content followed by undecayed yellow-poplar and red oak residues (Fig 6).

The mean and SD of the gross higher heating values of yellow-poplar and red oak were determined using a Parr oxygen bomb calorimeter (Tables 3 and 4), which were generally consistent with other reported values (Ince 1979; White 1987). The heating value showed no significant differences (P > 0.09) between sapwood and heartwood residues of 2007 harvest site between decayed (2005 – 2006) and undecayed (2007) logging residues. Higher heating values of yellow-poplar and red oak sapwood

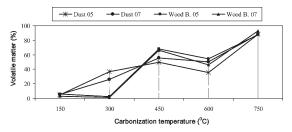


Figure 5. Gross higher heating value of yellow-poplar and red oak sapwood residues by year of harvest.

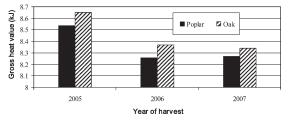


Figure 6. Carbonization of solid wood blocks (Wood B) vs wood dust (dust) of 2005 and 2007 harvested yellow-poplar wood.

residues of 2005 harvest were 3.2 and 3.5% higher than their 2007 sapwood residues, respectively. A t-test comparison between yellow-poplar and red oak residues failed to show any significant differences (P = 0.056), whereas Duncan multiple comparison test indicated that the 2005 residues were significantly different from 2006 – 2007 residues in heating value. It is evident from this study that the heating value of red oak wood was not significantly higher (about 1%) than yellow-poplar residues and that duration of residue on-site within 4 yr of harvest had a significant effect on the higher heating value of red oak and yellow-poplar residues (Fig 5).

Observed higher heating values of decayed residues of red oak and yellow-poplar were contrary to the expected result. It was expected that the reduction in holocellulose content from biodeterioration agents would indirectly lower the heating value of decayed wood residues. However, a more critical look at the chemistry of wood decay process also reveals that the reduction in holocellulose content caused a proportionate increase in high-calorific lignin content plus accumulated layers of dead biodeterioration organisms. The cell walls of wood decay fungi are composed of 80 - 90% high calorific polysaccharides with proteins, lipids, and polyphosphates (Madigan et al 2003). Lignin, with a heating value of 9.8 - 10.8 kJ, was reported to have a strong correlation to higher heating value of wood, whereas cellulose and hemicelluloses have a heating value of only 7.9 kJ (Baker 1983; White 1987). These additions to the lignin content could have resulted in

the slight increases in the higher heating values of decayed wood residues vs undecayed.

#### CONCLUSIONS

Our results indicated that logging residues of yellow-poplar and red oak were dried on-site to a moisture range of 7.4 - 39% as a result of the long cyclic exposure to humidity and temperature after 1 - 3 yr of harvest. A decreasing trend in sapwood-specific gravity with duration on-site from biodeterioration organisms was observed. Yellow-poplar sapwood-specific gravity was reduced by 15 and 26.5% on average after 2 yr (2006) and 3 yr (2005) of ground contact, respectively. Similarly, red oak-specific gravity for sapwood was lower than its heartwood by 26.6, 25.3, and 8.2% for 2005, 2006, and 2007 harvest years, respectively.

Chemical properties of yellow-poplar and red oak wood residues were less variable between heartwood and sapwood and across year of harvest, except in samples that experienced increased fungal decay resulting from length of exposure. Higher extractive and lignin content at the expense of lower holocellulose content was observed in decayed (2005 harvest) sapwood residues of yellow-poplar and red oak woods.

The range of values obtained for volatile and fixed carbon and ash content were in agreement with previous findings (Sjöström 1981; Demirbas 1997). There was about 80% volatiles, 20% carbon, and 1% ash content in both species regardless of the decay condition. The heating values showed no significant differences between sapwood and heartwood of decayed and undecayed residues. The heating value of red oak wood is not significantly higher (about 1%) than yellow-poplar residues, and the duration of residue on-site within 4 yr of harvest significantly affects the higher heating values of red oak and yellow-poplar residues.

On the basis of our chemical analysis, about 1.02 billion kg of sugars, 0.36 billion kg of lignin, and 0.06 billion kg of extractive content could be generated from 60% of the annually

generated logging waste of 2.41 billion kg dry wood residues in West Virginia. A 10-yr simulation to predict yellow-poplar wood loss resulting from the effect of environmental exposure and residue potential indicated an increase in biomass accumulation at a decreasing rate leading to over 50% reduction in total logging residue when compared with fresh residues. Assuming 60% of all residues can be economically transported, accumulated biomass has the potential to support five ethanol plants. Residue loss from decay points to a need for on-site storage facilities or prompt removal of logging residues from the forest site after 2 yr. There is also a need for complementary industries to consume wastes (about 83% loss of the original solid wood residues) generated from extractives, lignin, and solid fermentation substrates.

The residues of the two hardwood species used in this study can be used as feedstock or serve as substitute species for the production of fermentable sugars, lignin, and synthetic gases (a raw material for the Fisher Tropsch process) for the production biofuels, biochemical products, and electricity generation through direct combustion of wood owing to their comparable physical and heat-related properties. The close property similarities between red oak and yellow-poplar is a positive indication for effective utilization of logging waste resources in the Appalachian region for bioenergy.

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