CHEMICAL COMPOSITIONS OF FIVE 3-YEAR-OLD HARDWOOD TREES

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ABSTRACT

Contents of lignin, pentosan, holocellulose, and alpha-cellulose were determined on 3-year-old trees of autumn olive, black alder, black locust, eastern cottonwood, and sycamore. These plantations were established on marginal agricultural land in the Midwestern United States that was not suitable for food production. Test results indicated that chemical properties did vary among species, planting sites, spacing, and tree portion. Trees grown on upland sites gave significantly higher values for lignin, pentosan, and holocellulose content. The narrowly spaced trees gave higher values for pentosan content. The widely spaced trees gave higher values for lignin, holocellulose, and alpha-cellulose content. The mixture tree portion contained higher amounts of lignin. The wood portion contained more pentosan, holocellulose, and alpha-cellulose. Autumn olive had the highest lignin content. Sycamore had more pentosan and holocellulose. Black locust had the highest alpha-cellulose content. The results indicated that the five 3-year-old deciduous species examined could serve as a raw material for the rayon and polymer industries, as well as for liquid fuel.

Keywords: Cellulose, juvenile hardwoods, lignin, pentosan, plantations.

INTRODUCTION

Statement of problems

In recent years, an increasingly widespread shortage of raw material for wood, board, paper, and organic chemicals in North America has led to a search for new sources of fibers. It seems appropriate at this time to investigate the suitability of high yield, short-rotation, deciduous biomass as a substitute raw material for these important products. The use of juvenile wood for a raw material in the synthesis of organic chemicals has great potential. Woody biomass could produce polymers and chemicals, in many cases, using less costly, simplified chemical processes, if a continuous supply of raw material were available. Large deciduous biomass plantations could provide chemical industries with this supply (Goldstein 1981). Blankenhorn and coworkers (1992) reported that the use of short-rotation intensive culture (SRIC) biomass as a feedback for chemicals depends on the plantation productivity and the basic properties of the biomass. They also suggested that the wood tissue component, age, and parentage of the hybrid poplar (NE-388) would influence the chemical yields and processing parameters of the wood biomass. Wood

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and agricultural plant residues have been considered as "engineering materials" because they are economical, low in processing energy, and renewable. Biomass will make an important contribution to the problems of organic chemicals supply, as reported by Rowell (1992).

The conversion of biomass resources to polymeric materials, chemicals, and fuel can contribute to the growth of development of the nation's economy, according to Narayar (1992). Opportunities also exist for the cost-effective production of biobased materials and composite products (Chum and Power 1992; Rowell 1992).

As far as the economics of the biomass utilization is concerned, Strauss and coworkers (1988) evaluated the total cost of biomass supply system. They concluded that biomass from hybrid poplar plantation systems was not competitive with wood from native forests. In part, the added cost of plantation biomass was due to the proposed use of high agricultural site and land costs. In 1992, Goldstein reported that the technical feasibility of converting biomass into a variety of useful chemicals and fuels has been long established. The most important considerations affecting the ultimate large-scale conversion of biomass into chemicals and fuels are the cost and availability of the fossil fuels. At some time, the depletion of this resource will lead to a higher price and make renewable raw material fibers like biomass economically attractive.

A wide range of organic chemicals and fuel can be produced from the basic ligno-cellulose structure of woody biomass products that are obtainable from pentoses, cellulose, and lignin:

1. Pentoses (5-carbon sugars)
   - a.) Fermentation:
     Yeast (for production of vitamins, protein, and fat)
   - b.) Dehydration:
     Furfural (for plastic manufacturing)
   - c.) Hydrogenation:
     Polyols (chemical solvents and intermediates)
   - d.) Crystallization:
     Xylose (for furfural production)
2. Cellulose and Hexoses (6-carbon sugars)
   - a.) Fermentation:
     Alcohol (ethyl-, butyl-, isopropyl-); Polyols (glycerol; ethylene glycol, an antifreeze; propylene glycol); ketones (such as acetone for making explosives, nail polish, and many other products); and acids (acetic-, lactic-, butyric-).
   - b.) Dehydration and hydrolysis:
     Hydroxymethylfurfural, levulinic acid (chemical intermediates)
   - c.) Hydrogenation:
     Glycerol and other alcohols
   - d.) Crystallization:
     Glucose (for alcohol production; also a human nutrient)
3. Lignin
   - a.) Hydrolysis:
     Phenolic mixture (for production of synthetic adhesives)
   - b.) Hydrogenation:
     Benzene and other aromatics (for production of solvents, dyes, and other organic compounds)
   - c.) Hydroalkylation:
     Cresylic acids (for production of hydroxyacetophenones)

Other synthetic fibers and polymers that can be derived from wood biomass include: nylon from furfural, rayon and photographic films from alpha-cellulose, and vanillan and adhesives from lignin (Goldstein 1981). The chemical makeup of wood varies greatly by species, age, and portion of the tree according to Chow and coworkers (Chow et al. 1980, 1987; Chow and Lucas 1988; and Chow and Rolfe 1989). The chemical makeup in turn affects the tree utilization for various uses. It is therefore essential to determine and characterize species that will give high yields when planted on a short-rotation silvicultural system, and have desirable chemical composition for use as feed stock for chemicals production.

A previous study (Lee 1981) indicates that favorable hardwood species for this purpose are autumn olive (*Elaeagnus umbellata* Thunb.), black alder (*Alnus glutinosa* L.), black locust (*Robinia pseudoacacia* L.), eastern cottonwood (*Populus deltoides* Bartr.), and sycamore (*Platanus occidentalis* L.). Data are needed concerning the effects of silvicultural characteristics of the plantation on the chemical composition, for sound economic analysis of the utilization of these species.

Objective

The primary objective of this study was to determine the lignin, hollocellulose, alpha-cellulose, and pentosan content of five 3-year-old short-rotation hardwood species, grown by variable silviculture characteristics of the plantation. The effects of species, tree portion, planting space, and planting site on the chemical properties of the juvenile hardwoods were determined.

EXPERIMENTAL MATERIAL, DESIGN AND TEST METHODS

Material and sample preparation

Bundles of whole tree specimens were received from plantation sites at the Dixon Springs Agriculture Center, southern Illinois. The trees were harvested and bundled according to species, site, and spacing variables of the growth plots. All trees were 3 years old. All five species were grown on both bottomland and upland sites, and with both narrow and wide spacings. The wide spacing indicated in this study meant 30.5 × 45.7 cm, and the narrow meant 23 × 23 cm.

Weights of each bundle were recorded. Branchwood was then removed from each main stem, and the branchwood and stemwood portions were each weighed for determination of the branch to stemwood ratio.

To prepare the wood portion, bark was removed from sections of the base, center, and top of randomly chosen stems of each bundle. These bark-free stem sections were then cut into small cross-sectional disks, and ground in a Wiley mill to pass a 60-mesh screen (250-μm sieve). For the mix portion, sections of stemwood from the base, center, and top were cut and ground to pass a 60-mesh screen. Randomly chosen branchwood was then ground to particles and mixed with the stemwood particles in the original stem to branch ratio.

Experimental design

A Randomized Complete Block (RCB) design was used in the factorial analysis to determine the effects of the silvicultural treatment combinations on each dependent variable (lignin, pentosan, holocellulose, and alpha-cellulose contents). The treatments or independent variables were site (factor A), spacing (factor B), wood portion (factor C), and species (factor D).

Site:
- A1 = bottomland
- A2 = upland

Spacing:
- B1 = narrow (23 × 23 cm)
- B2 = wide (30.5 × 45.7 cm)

Tree portion:
- C1 = mixture of bark, branches, and stemwood
- C2 = wood

Species:
- D1 = autumn olive (*Elaeagnus umbellata* Thunb.)
- D2 = black alder (*Alnus glutinosa* L.)
- D3 = black locust (*Robinia pseudoacacia* L.)
- D4 = eastern cottonwood (*Populus deltoides* Bartr.)
- D5 = sycamore (*Platanus occidentalis* L.)

Thus the overall analysis of the RCB was 2 × 2 × 2 × 5 factorial, for each dependent variable.

The following linear model for the RCB was used for explaining sources of variation:

$$\begin{aligned} Yijklm = {} & \mu + Ri + Aj + Bk + ABjk + Cl \\ & + ACjl + BCkl + ABCjkl + Dm \\ & + ADjm + BDkm + CDlm \\ & + ABDjkm + ACDjlm + BCDklm \\ & + ABCDjklm + \epsilon ijklm \end{aligned}$$

where,

TABLE 1. *Specific gravity and moisture content of test material.*

Species		Specific gravity[a] Stem wood	Specific gravity[a] Stem with wood bark	Moisture content Stem wood	Moisture content Stem wood with bark
Autumn olive	NB[b]	0.72	0.62	7.3	7.6
	NU	0.69	0.70	7.1	7.4
	WB	0.67	0.71	8.2	9.3
	WU	0.72	0.78	10.6	15.0
Black alder	NB	0.47	0.52	9.2	10.1
	NU	0.46	0.52	7.4	7.8
	WB	0.44	0.55	7.9	8.6
	WU	0.43	0.48	7.0	8.5
Black locust	NB	0.52	0.62	12.8	12.6
	NU	0.61	0.69	9.5	8.4
	WB	0.54	0.53	10.8	10.4
	WU	0.46	0.55	10.2	9.5
Eastern cottonwood	NB	0.39	0.42	8.0	8.2
	NU	0.43	0.43	7.0	7.0
	WB	0.39	0.48	8.6	8.1
	WU	0.38	0.43	10.1	9.1
Sycamore	NB	0.70	0.66	7.9	8.0
	NU	0.55	0.52	9.5	9.3
	WB	0.50	0.52	10.2	11.3
	WU	0.52	0.51	8.0	9.5

[a] Based on oven-dry weight and air-dry volume.
[b] N = narrow spacing (23 × 23 cm), W = wide spacing (30.5 × 45.7 cm), B = bottomland, U = upland.

Yijklm = any observed value for a chemical property
μ = overall mean
Ri = block effect (replication)
Aj = site effect
Bk = spacing effect
Cl = wood portion
Dm = species effect
ϵijklm = experimental error

and

i = 1–6 replications
j = 1–2 levels of A
k = 1–2 levels of B
l = 1–2 levels of C
m = 1–5 levels of D

All combinations of letters in the model represent interaction effects of the independent variables.

All statistical analyses were carried out using computer software procedures described in the Statistical Analysis System (SAS) for Linear Models (SAS 1992). Procedures used included General Linear Models for the factorial analysis, Duncan's Multiple Range test for multiple comparisons among means, and the least significant difference (LSD) procedure for the *t*-test multiple comparisons between means.

Test methods

All experimental procedures were carried out according to the American Society for Testing and Materials (ASTMD 1103, D 1104, and D 1106; 1982) and the Technical Association of the Pulp and Paper Industry (TAPPI 1992). Six tests were run for each combination of independent variables represented in this study.

RESULTS AND DISCUSSION

Table 1 shows the moisture content and specific gravity of sample material.

Lignin content

Lignin is defined as the insoluble residue remaining after complete hydrolysis of the polysaccharide portion of wood, when extractives have been previously removed. Lignin contents for North American hardwoods range from about 17 to 25% (Brown et al. 1952). Working with commercial lumber of species tested in this study, an average lignin content of about 24% was found by Lee (1981). Lee also found that lignin content did not depend on age of the tree, but did depend on tree portion. Bark contains about 6% more lignin than the wood.

Lignin contents for all combinations of independent variables are shown in Table 2. Lignin contents for the wood portion of these juvenile woods were 21.0, 21.6, 23.4, 24.9, and 25.8% for black locust, sycamore, black alder, autumn olive, and eastern cottonwood, respectively. The mix portion of the juvenile woods provided higher values of 22.3, 22.7, 26.2, 29.1, and 30.0%, for black locust, sycamore, eastern cottonwood, autumn olive, and black alder, respectively. Lignin content values

TABLE 2. *Chemical properties of five hardwood species.*

Species	Portion	Site	Spacing	Lignin %	Pentosan %	Holocellulose %	α-cellulose %
Autumn olive	Mixture	B[a]	N[b]	28.4	19.2	67.2	35.4
			W	29.0	18.8	64.2	33.9
		U	N	31.1	18.4	68.3	34.8
			W	28.1	18.0	67.1	34.5
	Wood	B	N	24.6	19.4	75.1	36.4
			W	24.2	19.6	78.2	40.8
		U	N	25.5	20.3	75.8	38.9
			W	25.4	18.9	73.0	38.4
Black alder	Mixture	B	N	28.8	17.8	62.1	30.2
			W	30.8	17.9	70.3	33.8
		U	N	27.3	18.6	73.0	35.4
			W	33.3	18.2	59.7	29.1
	Wood	B	N	22.2	19.7	76.5	35.4
			W	25.3	20.6	75.2	35.2
		U	N	22.3	20.2	79.5	38.1
			W	23.9	20.0	74.6	35.9
Black locust	Mixture	B	N	22.7	16.5	69.4	38.2
			W	22.1	15.8	71.0	38.8
		U	N	23.1	17.5	67.7	36.8
			W	21.3	16.2	72.0	40.1
	Wood	B	N	19.8	17.1	77.2	42.3
			W	22.0	17.6	76.8	42.0
		U	N	18.9	17.4	75.0	42.6
			W	23.4	17.3	78.0	41.8
Eastern cottonwood	Mixture	B	N	24.1	16.2	64.1	32.2
			W	26.3	15.7	71.3	35.1
		U	N	27.2	16.3	68.3	34.9
			W	27.3	16.1	65.8	30.3
	Wood	B	N	24.2	17.7	70.3	34.4
			W	27.0	16.4	79.7	40.9
		U	N	25.7	18.8	76.6	39.9
			W	26.3	19.1	74.4	35.7
Sycamore	Mixture	B	N	22.4	20.0	69.7	32.1
			W	22.6	19.2	76.5	35.3
		U	N	23.2	19.6	79.1	36.6
			W	22.7	19.7	76.9	34.1
	Wood	B	N	19.4	20.1	76.9	33.6
			W	22.0	19.8	79.1	37.0
		U	N	22.3	20.0	76.7	34.5
			W	22.5	20.1	76.9	34.0

[a] B = Bottomland, U = upland, [b] N = Narrow, W = wide.

of the mixture portion exceed the average values of mature hardwoods because the test samples contained both bark and wood substances. In addition to lignin, bark contains polyphenolic and tannin materials that are acid-soluble and would be calculated as lignin in conventional Klason lignin determinations.

In the analysis of variance, the site and portion, and the site and spacing and portion interactions were not significant (Table 3). All other terms in the model were significant and important in explaining variation. The coefficient of variation ranges from 0.3 to 5.6% (Table 2).

TABLE 3. *Factorial analysis.*

Independent variable	Degree of freedom	Lignin	Pentosan	Holocellulose	Alpha-cellulose
A (Site)	1	HS	HS	HS	N
B (Spacing)	1	HS	HS	HS	HS
A × B	1	HS	N	HS	HS
C (Wood Portion)	1	HS	HS	HS	HS
A × C	1	N	HS	HS	N
B × C	1	HS	HS	N	HS
A × B × C	1	N	S	HS	N
D (Species)	4	HS	HS	HS	HS
A × D	4	HS	HS	HS	HS
B × D	4	HS	HS	HS	HS
A × B × D	4	HS	HS	HS	HS
C × D	4	HS	HS	HS	HS
A × C × D	4	HS	HS	HS	HS
B × C × D	4	HS	HS	HS	HS
A × B × C × D	4	HS	HS	HS	HS

HS = significant difference at 1% level; S = significant at 5% level, N = no significance at 5% level.

Pentosan content

Pentosans are the five carbon sugar units contained in the hemicelluloses of wood and are composed mainly of xylose and arabinose. Mature North American hardwoods contain an average of about 21.4% pentosans (Wise and Jahn 1952). Table 2 shows that pentosan contents for the wood portion were 17.4, 18.0, 19.5, 20.0, and 20.2% for black locust, eastern cottonwood, black alder, autumn olive, and sycamore, respectively. The coefficient of variation ranges from 0.38 to 2.68%.

In the analysis of variance, all factors and interactions were significant factors in explaining variation in the model with the exception of the site and spacing, and the site and spacing and portion interactions (Table 3). Most important in explaining variation in the model were the portion and the species variables.

Holocellulose content

Hollocellulose contents of mature North American hardwoods range from about 75.0 to 82.5% (Timell 1957). Table 2 shows that holocellulose content for the wood portion of these juvenile woods were 75.2, 75.5, 76.4, 76.7, and 77.4% for autumn olive, eastern cottonwood, black alder, black locust, and sycamore, respectively. All of these values for wood portion are similar to the range for mature hardwoods. The mix portions gave lower values of 66.3, 66.7, 67.4, 70.0, and 75.6% for black alder, autumn olive, eastern cottonwood, black locust, and sycamore, respectively. The mixture portion contains less holocellulose due to the inclusion of the bark, which contains large amounts of lignin. The coefficient of variation ranges from 0.29 to 2.43%.

For the variable of wood portion, the mean for the wood portion was significantly higher than the mixture with values of 76.3 and 69.2%, respectively. For the variable species, the mean for sycamore was significantly different than for the other four with a value of 76.5%. In the analysis of variance (Table 3), the spacing and portion interaction were not significant factors.

Alpha-cellulose content

Alpha-cellulose contents of mature North American hardwoods generally range from about 45 to 50% of the total wood substance (Timell 1957). Table 2 shows that alpha-cel-

TABLE 4. *Summary of Duncan's multiple range test by site, spacing, and portion.*

	Site		Spacing		Portion	
Lignin content	A2	A1	B2	B1	C1	C2
Pentosan content	A2	A1	B1	B2	C2	C1
Holocellulose content	A2	A1	B2	B1	C2	C1
Alpha-cellulose content	A2	A1	B2	B1	C2	C1

[1] Significance level = 0.05, degrees of freedom = 195.
[2] Means with same line are not significantly different.
[3] Left to right are highest to lowest species means.
[4] A1 = bottomland, A2 = upland.
[5] B1 = Narrow, B2 = wide.
[6] C1 = Mixture, C2 = wood.

lulose content of the wood portion of these juvenile woods ranged from a low of 34.8% for sycamore, to a high of 42.2% for black locust. The mixture portions contained less alpha-cellulose and ranged from a low of 32.1% for black alder to a high of 38.5% for black locust. These values for alpha-cellulose content of juvenile hardwoods are much lower than accepted values for mature hardwoods.

There was no significant difference between upland and bottomland site with values of 36.2 and 36.1%, respectively. (Tables 3 and 4). All species means varied significantly from each other with values of 34.1, 34.7, 35.0, 36.6, and 40.3% for black alder, sycamore, eastern cottonwood, autumn olive, and black locust, respectively. The coefficient of variation ranges from 0.1 to 4.2%. In the analysis of variance (Table 3), the site factor, the site and portion, and the site and spacing and portion interactions were not significant in explaining variation in the model.

SUMMARY

1. From the measurements of this study, we can conclude that all of the independent variables—planting site, tree spacing, wood material portion, and species—caused significant variations on the chemical properties of five species of 3-year-old juvenile hardwoods.
2. In the comparison of bottomland and upland sites (Table 4), all means of dependent variables, with the exception of the alpha-cellulose contents, varied significantly. Trees grown on upland sites gave significantly higher values for lignin content, pentosan content, and holocellulose content.
3. In comparison of narrowly spaced and widely spaced trees (Table 4), the narrowly spaced trees gave significantly higher values for pentosan content. Widely spaced trees gave significantly higher values for lignin content, holocellulose content, and alpha-cellulose content.
4. In the comparison of the wood material portion (Table 4), the mixture portions contained significantly higher amounts of lignin. The wood portion contained significantly higher amounts of pentosans, holocellulose, and alpha-cellulose.
5. In comparisons among species (Table 5), autumn olive had the highest lignin content. Sycamore had the highest contents of pentosans and holocellulose. Black locust had the highest alpha-cellulose content.
6. The material balance for the wood analysis is satisfactory as far as lignin, plus holocellulose, is concerned. However, in considering alpha-cellulose, pentosan, and holocellulose, there is more than 10% of the holocellulose unaccounted for. This may represent hexosan, glucuronic acid, and pectic materials in the juvenile wood. Further study is needed to characterize this unidentified portion of the juvenile wood.
7. Results from this study show that these five juvenile deciduous species have chemical compositions that should be useful for producing fiber and chemicals, when grown under intensive care in central and southern Illinois sites. The best species of these five tested 3-year-old trees seems to be black locust, which could serve as a raw material for chemical industry, as well as for fuel or energy generation.

TABLE 5. *Duncan's multiple-range test by species.*

Lignin content	S1	S2	S4	S5	S3
Pentosan content	S5	S1	S2	S4	S3
Holocellulose content	S5	S3	S2	S4	S1
Alpha-cellulose content	S3	S1	S4	S5	S2

[1] Significance level = 0.05, degrees of freedom = 195.
[2] Means with same line are not significantly different.
[3] Left to right are highest to lowest species means.
[4] S1 = Autumn olive, S2 = Black alder, S3 = Black locust, S4 = Eastern cottonwood, S5 = Sycamore.

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