

# ENERGY VALUE OF PARAQUAT-TREATED AND RESIN-SOAKED LOBLOLLY PINE<sup>1</sup>

*Susan V. Kossuth*

Supervisory Research Plant Geneticist/Physiologist  
USDA Forest Service, Southeastern Forest Experiment Station, Gainesville, FL 32611

*Donald R. Roberts*

Research Plant Physiologist, Retired  
USDA Forest Service, Southeastern Forest Experiment Station, Olustee, FL 32072

*Jacob B. Huffman*

Associate Professor of Forest Products

and

*Shih-Chi Wang*

Assistant Research Scientist in Wood Science  
School of Forest Resources and Conservation, University of Florida, Gainesville, FL 32611

(Received March 1983)

## ABSTRACT

With a basal injector, loblolly pines were treated with 5% paraquat cation (weight/weight basis) and harvested after 18 months. The resin acid, turpentine, moisture content (MC), and energy value were measured in three bolts of the stem. In bolt 1, the first 152 cm above the injection site, the increase in resin acids was 392% and in turpentine, 564%. Within the whole stem (the first two 152-cm bolts and the third bolt to a 7.6-cm inside-bark diameter), resin acids and turpentine increased 203 and 296%, respectively. Moisture content was reduced 9%, 8%, and 8% in bolts 1, 2, and 3, respectively. Turpentine from treated and untreated trees had an average heating value of 19,369 cal/g. When weighted for volume, net energy content was 7.8% greater for treated than control trees because of the increase in resin, including turpentine and the lowered MC.

*Keywords:* Oleoresin, resin soaking, turpentine, resin acids, paraquat, energy.

As energy prices soar and supplies become limited, the interest in growing trees for fuel has increased (Bente 1979; McAlpine et al. 1966; Szego et al. 1972; Young 1972). Considerable research has been conducted to study increases in resin of pines after treatment with paraquat (LRCC 1974–1979). However, no studies have been made to measure the caloric content of resin-soaked pine. The tremendous increase in resin, especially in the first 3 m of the stem above the treatment site, should result in large increases in the caloric value of treated trees.

The objectives of this study were to measure resin acid, moisture, turpentine, and caloric content of stem wood of paraquat-treated loblolly pine (*Pinus taeda* L.).

<sup>1</sup> Appreciation is extended to John Munson, Junior Broomfield, Gary Holmes, Kimberly Horgan, Southeastern Forest Experiment Station, Olustee, FL 32072, and Lyn Brown, School of Forest Resources and Conservation, University of Florida, Gainesville, FL 32611 for technical assistance.

This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate state and/or federal agencies before they can be recommended.

TABLE 1. Analysis of changes in mass of loblolly pine stem components 18 months after treatment with 5% paraquat cation (weight/weight basis).<sup>a</sup>

Stem portion	Resin acids			Turpentine			Wood		Water	
	Treated	Un-treated	Increase	Treated	Un-treated	Increase	Treated	Un-treated	Treated	Un-treated
	kg/m <sup>3</sup>		%	kg/m <sup>3</sup>		%	kg/m <sup>3</sup>		kg/m <sup>3</sup>	
Bolt 1 <sup>b</sup>	54.1*	13.8	392	17.5*	3.1	564	621*	621	444*	485
Bolt 2	27.4*	9.2	298	9.4*	1.5	626	611*	615	493*	539
Bolt 3	11.8	11.3	4	2.9	2.4	121	548	544	530	575
Wt. avg. <sup>c</sup>	23.4*	11.5	203	7.1*	2.4	296	574*	574	505*	518

<sup>a</sup> Data analyzed by Scheffé's test.

<sup>b</sup> Bolt 1 = first 152 cm, Bolt 2 = second 152 cm above the treatment site, and Bolt 3 = the remaining merchantable stem to a 7.6-cm inside-bark diameter.

<sup>c</sup> Weighted according to volume of each bolt.

\* Significantly different from control at 0.05 level.

#### MATERIALS AND METHODS

Plantation-grown loblolly pines, approximately 20 years old, near Aiken, South Carolina, were injected between April and July 1977, with 5% paraquat cation (weight/weight basis). This was done in a 3.8-cm-wide slash through the bark every 12.7 cm around the trees. Fifteen injected and fifteen similar but untreated trees randomly assigned as controls were harvested for analysis after 18 months. The trees were felled and crosscut into 3 bolts: bolt 1 was the first 152 cm (60 in.) above the injection site, bolt 2 the second 152 cm (60 in.), and bolt 3 the remaining merchantable stem to a 7.6-cm (3-in.) inside-bark diameter. A 2.5-cm (1-in.) stem disk was cut every 30.4 cm (12 in.) of the tree length, and the disks were combined on a bolt basis (i.e., 5 disks each from bolts 1 and 2, and a variable number of disks from bolt 3, depending on the total length of this bolt). The bark was peeled from each disk and the combined disks were first ground in a wood grinder to pass a 0.5-cm mesh screen for chemical analysis and then in a Wiley Mill to pass a 0.6-mm mesh screen for caloric determinations. Disks and chips were frozen to retard loss of volatiles between all stages of processing samples.

Turpentine was determined by a modified procedure of Pulp Chemicals Association (Kossuth and Munson 1980). An internal standard of 250  $\mu$ l n-tetradecane was added to each 50-g sample of wood chips, which were digested in 0.5 N sodium hydroxide and refluxed for 90 min. The volatiles, including the internal standard, were condensed and analyzed by gas-liquid chromatography. Resin acids were determined by a modified method of Shepard (1975) employing xylene extraction and titration to determine free acid content. Analyses of variances and Scheffé's test were used to test for differences among bolts.

Heats of combustion were determined with an adiabatic oxygen bomb calorimeter with automatic jacket controls, following the general procedures of Howard (1973). Two duplicate ground-wood samples, each approximately 0.5 g, were combusted. If the duplicates differed by 1%, additional samples were combusted until consistent values were obtained. Heat value of turpentine was measured for samples contained in closed capsules, which were weighed immediately before combustion.

Specific gravity of the unextracted samples was obtained by volume displacement in water of a weighed sample of the chips used for resin acid and turpentine analysis.

TABLE 2. Gross energy value and distribution in stems of loblolly pine 18 months after injection with 5% paraquat cation (weight/weight basis).<sup>a</sup>

Stem portion	Caloric value							
	Resin acid plus wood				Total (includes turpentine)			
	Treated		Untreated		Treated		Untreated	
	<i>kcal/kg</i>							
Bolt 1 <sup>b</sup>	5,039*		4,698		5,173*		4,727	
Bolt 2	3,823*		4,652		4,904*		4,666	
Bolt 3	4,701		4,670		4,732		4,695	
Wt. avg. <sup>c</sup>	4,809*		4,663		4,875*		4,686	

  

	Volumetric value <sup>d</sup>								
	Resin acids plus wood			Turpentine			Total		
	Treated	Untreated	Diff.	Treated	Untreated	Diff.	Treated	Untreated	Diff.
	<i>kcal × 10<sup>3</sup></i>		%	<i>kcal × 10<sup>3</sup></i>		%	<i>kcal × 10<sup>3</sup></i>		%
Bolt 1	135,062*	118,009	14	7,195*	1,275	565	142,257*	119,373	19
Bolt 2	100,298*	94,573	6	3,177*	507	627	103,475*	95,080	9
Bolt 3	304,512	299,804	2	3,477	2,787	21	307,989	302,681	2
Stem total <sup>e</sup>	539,872*	512,476	5	13,849*	4,659	297	553,721*	517,135	7

<sup>a</sup> Data analyzed by Scheffé's test.<sup>b</sup> Bolt 1 = first 152 cm, Bolt 2 = second 152 cm above treatment site, and Bolt 3 = remaining merchantable stem to a 7.6-cm inside-bark diameter.<sup>c</sup> Weighted according to the volume of each bolt.<sup>d</sup> Calorimetric measurements times quantity of components per bolt.<sup>e</sup> Untreated volumes adjusted to the same as treated-tree volumes.

\* Significantly different from control at 0.05 level.

Percent resin acids, turpentine, and moisture on a weight basis were obtained in the extraction processes. The quantities of resin acid and turpentine in the wood samples were obtained by using the unextracted specific gravities of 0.64, 0.63, and 0.56 for treated bolts 1, 2, and 3; and 0.69, 0.65, and 0.56 for control bolts. Bolt volume was calculated as a frustrum of a cone from measurements of height and diameter inside bark at harvest.

Gross energy yield (kilocalories) per bolt was obtained by multiplying the kcal/m<sup>3</sup> for each component by the bolt volume. Quantitative determinations of resin acids and turpentine, and caloric value for control tree yield, were adjusted to reflect the same volume as treated trees.

The energy loss resulting from combustion in a commercial process was determined by values from Saeman (1977). Reduction of heat value due to the presence of moisture was 0.28% for every percent green weight moisture content (MC). Heat lost due to evaporation of water formed by hydrogen combustion and flue gasses was 7.67 and 8.02%, respectively.

#### RESULTS

In bolts 1 and 2, resin acid content showed a 392 and 298% increase over control bolts and a 564 and 626% increase in turpentine over controls (Table 1).

Caloric content of extracted turpentine fractions was similar in all bolts, averaging 19,369 cal/g from 25 determinations. Treated tree energy values of dry wood (resin acids plus wood) obtained from bolts 1 and 2 were significantly greater (0.05 level) than those of the controls (Table 2). Bolt 3 of the treated trees also

TABLE 3. Net energy yield and distribution on a green-weight basis of whole stem components of loblolly pine 18 months after treatment with 5% paraquat cation (weight/weight basis).

Stem portion	Net energy yield <sup>a</sup>		
	Treated	Control <sup>b</sup>	Difference
	<i>kcal</i> × 10 <sup>3</sup>		%
Bolt 1 <sup>c</sup>	104,398	86,208	12
Bolt 2	74,720	67,836	10
Bolt 3	217,841	214,095	2
Total	396,959	368,138	8

<sup>a</sup> Calorimetric measurements times quantity of components per bolt.

<sup>b</sup> Control volumes adjusted to be the same as treated-tree volumes.

<sup>c</sup> Bolt 1 = first 152 cm, Bolt 2 = second 152 cm above treatment site, and Bolt 3 = the remaining merchantable stem to a 7.6-cm inside-bark diameter.

had higher energy values, but they were not significantly greater than those of the controls. On a whole stem basis, the gross energy value of the treated trees was 7% higher than for control trees. Net energy yield (effective heating value) of whole stems of treated trees was 8% greater than for control trees (Table 3). This was due to the large increases in resin and a decrease in MC in bolts 1 and 2 of the treated trees.

#### DISCUSSION AND CONCLUSIONS

The combined effect of lower MC coupled with higher resin yields (Table 1) significantly increased the net energy value of treated loblolly pines, especially in bolts 1 and 2. Desiccation is listed on the marketing label of paraquat as one of the effects of this contact herbicide, and in this study, moisture loss approximated the increase in resin. The desiccation greatly increased the net energy of the stem wood because less energy was lost in the combustion process because of moisture in the raw material.

Because paraquat is a highly toxic herbicide, some reduction in volume growth due to death of the cambium might be expected in treated trees. An earlier study (Nix 1979) showed volume growth reduction of 31 and 21% in the first and second years after loblolly pines were treated using one-half-tree circumference by 2.54-cm bark streak sprayed to runoff with 4% paraquat. This was similar to findings in slash pine (Squillace and Moyer 1976). Further studies are needed to clarify expected volume growth loss with various kinds of treatment and concentrations of the chemical so that per acre yields of wood and potential energy values can be calculated.

In this study we found a 12% higher net energy value in paraquat-treated 20-year-old loblolly pines than controls in bolt 1, and somewhat lesser values in bolts 2 and 3. When optimum treatment procedures are known, growth reductions may be low enough that this high energy per unit volume in the first 3 m could be of value for fuel. For example, small wood-fueled gasifiers could utilize the first 300 cm and would then need to be refueled less often.

#### REFERENCES

- BENTE, P. F., ed. 1979. Bio-energy directory. Bio-Energy Council, Washington, DC. 533 pp.  
 HOWARD, E. T. 1973. Heat of combustion of various southern pine materials. Wood Sci. 5:194-197.

- KOSSUTH, S. V., AND J. W. MUNSON. 1980. Automated terpene analysis with an internal standard. *Tappi* 64(3):174-175.
- LIGHTWOOD RESEARCH COORDINATING COUNCIL. 1974-1979. Sponsored by Pulp Chemicals Association in cooperation with USDA Forest Service, Southeastern Forest Experiment Station, Asheville, NC. 6 vol.
- MCALPINE, R. G., C. L. BROWN, A. M. HERRICK, AND H. E. RUARK. 1966. "Silage" sycamore. *Forest Farmer* 26(1):6-7, 16.
- NIX, L. E. 1979. The effects of paraquat treatment on height growth, branch extension, and cambial activity of loblolly pine. Pages 21-27 in Mary H. Esser, comp./ed. Sixth Annual Lightwood Research Conference Proceedings. Pulp Chemical Association in cooperation with USDA Forest Service, Southeastern Forest Experiment Station, Asheville, NC.
- SAEMAN, J. F. 1977. Energy and materials from the forest biomass. Pages 153-158 in J. W. White and W. McGrew, eds. Symposium Papers, Clean Fuels from Biomass and Wastes, January 25-28. Institute of Gas Technology, Orlando, FL.
- SHEPHARD, C. 1975. Analytical procedure for determining the extractions of paraquat treated trees. Pages 78-83 in Robert N. Stone, ed. Lightwood Research Coordinating Council Proceedings, January 22-23, Jacksonville, FL. Chevron Chemical Co., Box 160, Ocoee, FL.
- SQUILLACE, A. E., AND E. MOYER. 1976. Genetic and environmental variation of induced resin soaking in slash pine—Second-year results. Pages 93-101 in Mary H. Esser, comp./ed. Second Annual Lightwood Research Conference Proceedings. Pulp Chemicals Association in cooperation with USDA Forest Service, Southeastern Forest Experiment Station, Asheville, NC.
- SZEGO, G. C., J. A. FOX, AND D. R. EATON. 1972. The energy plantation. Interscience Energy Conversion Engineering Conference, Seventh Conference, Proc. Paper 729168. San Diego, CA. 210 pp.
- YOUNG, H. E. 1972. Woody fiber farming: An ecologically sound and productive use of right-of-ways. University of Maine, School of Forest Resources, Orono, ME. 19 pp.