THE EFFECT OF HIGH PRESSURE HYDROGENATION ON SOUTHERN PINE BARK CHEMISTRY

Malcolm D. MacPeak and *Leonard F. Burkart*

Assistant Professor, and Professor, Wood Science
School of Forestry
Stephen F. Austin State University
Nacogdoches, TX 75962-6109

ABSTRACT

Whole bark, extracted bark, and the extracted bark phenolic acids were hydrogenated using a Raney-nickel catalyst and a catalyst to acceptor weight ratio of 0.75:1. The phenolic acids were more resistant, requiring a 1:1 weight ratio. Primary reaction products of bark were water-soluble compounds that appeared to be lower alcohols, substituted alcohols, and diols. Reaction products of the bark phenolic acids were not characterized. More work is required to separate and identify with certainty the constituents of the water-soluble fraction before the significance of this research can be evaluated. None of the products found appear to be formed in sufficient quantity or have chemical structures that would make the process economically feasible. Formation of a strong bark-catalyst complex made catalyst recovery difficult.

Keywords: Hydrogenation, bark chemistry, hydrogenolysis, phenolic acids.

INTRODUCTION

The energy crisis of the mid 1970s indicated that substitute sources of energy and chemical feed stocks should be explored. Renewable resources such as wood and bark offer a partial alternative to fossil fuels in uses such as fuel, fuel additives or extenders, or as substitutes for chemical feed stocks.

Hall (1971) pointed out that by the 1970s the chemical utilization of bark in the United States had largely ceased. That large quantities of bark were available for utilization has been documented. The amounts appear sufficient to sustain an active, high production chemical utilization program if one were developed. Sarles (1973) estimated that the bark produced by the forest products industry nationwide amounts to some 14 million dry tons annually, with about 6.2 million tons being produced in the southern states. Gedney (1971) estimated the bark produced annually in the three Pacific Coast states to be 437 million solid cubic feet, and Martin (1969) estimated a volume of 250 million cubic feet for the southern states. Sarles (1973) and Gedney (1971) estimated that 30 and 45%, respectively, of these estimated quantities were being wasted entirely and were being disposed of by

burning or dumping, the remainder being used primarily for fuel. Inefficient burning as fuel was used as a convenient method of bark disposal, thus inflating the fuel use values making the waste estimates conservative.

The presence of chemicals in tree bark is well documented (Ross 1966), but the total chemistry of bark remains obscure since most of the work has concerned itself with extractives appearing to have commercial promise (Nickles and Rowe 1962). The purpose of this research was to determine if bark or a bark fraction could be chemically altered so as to produce compounds having application as fuels, fuel extenders, or chemical feed stocks.

METHODS AND MATERIALS

Aside from pyrolysis, the literature is devoid of references to the drastic chemical alteration of bark or its fractions and the resulting chemistry. Wood and lignin have been exposed to a multitude of chemical treatments. After examining the work of Harris et al. (1938), Hrutfiord (1971), Pepper and Hagerman (1954), and Pepper and Steck (1963) high pressure hydrogenation was selected as a treatment that might produce the desired results in terms of products and percentages. Based on the literature, Raney-nickel was selected as a catalyst with a 50:50 mixture v/v of dioxane-water as the reaction solvent. Other solvents such as alcohols are also appropriate, but ethoxylation reactions were reported by Pepper and Hibbert (1948) when using ethanol. Catalyst preparation followed the method of Monzingo (1955), with modifications suggested by Fieser and Fieser (1967). Catalyst to acceptor weight ratios of 0.75:1 were found satisfactory for bark, but a 1:1 ratio was required for the phenolic acid fraction. An initial hydrogen pressure of 68 atmospheres was necessary to promote hydrogenation. Temperatures in excess of 231 C were required, however, temperatures above 250 C tended to produce carbonization and were avoided. The reaction appeared to go to completion if the temperature was held above 231 C for a period slightly exceeding five hours, which agrees well with the time period published in the literature for wood.

Bark was selected off the bark chain at a sawmill located in San Augustine, Texas. Approximately equal volumes of bark were picked from all sizes of logs as they passed through the debarker so as to obtain a cross section of the logs being processed. The species mix was most likely loblolly pine (*Pinus taeda* L.) with smaller volumes of shortleaf pine (*Pinus echinata* Mill.). The bark was stripped of all inner bark and ground to pass a 40-mesh (0.42-mm) screen. Samples taken from the material passing the 40-mesh screen indicated that about 35% of this material would pass an 80-mesh (0.177-mm) screen. After grinding and screening, the bark was allowed to equilibrate with the laboratory atmosphere. After equilibration, moisture content samples were taken and the remainder sealed in plastic jars.

In the initial phase of the investigation, the phenolic acid fraction was considered to be a likely substrate since it is the largest single fraction of bark. Depending on species, dilute base (1% NaOH) will remove nearly 50% of the dry bark weight with about one-half of this weight being the phenolic acids. Extraction of whole bark was performed using a one-hour reflux in 1% NaOH as described by McGinnis and Parikh (1975). Negative hydrogenation results with phenolic acids extracted in this manner lead to the investigation of other base extraction procedures such as soaking under ambient conditions for varying time periods or soaking at refrigerated temperatures.

Failure of the phenolic acid fraction to react prompted the investigation to turn to bark as a substrate. It was found to react readily under certain conditions, and as a result both whole and extracted bark were used as substrates. The extracted bark (EB) was prepared by extracting with alcohol-benzene for 48 h in a Soxhlet extractor, followed by air-drying and cold water extraction for 72 h with one water change and intermittent stirring. The extracted bark was equilibrated and stored using previously described procedures.

An experiment was designed wherein three extracted bark (EB) samples and three whole bark (WB) samples were hydrogenated along with three control samples from each type of bark. The control samples were exposed to the same conditions of temperature, pressure, initial hydrogen pressure, and solvent as the test samples with the exception that the catalyst was omitted. This design gives a total of 12 samples, which were numbered, and the order of treatment was randomly selected to eliminate any bias that might be introduced using nonrandom procedures. A constant sample weight of 20 g was used for all samples. One sample designated WBF 01 was made up of that portion of the bark passing an 80-mesh screen after having been ground to pass a 40-mesh screen. It was suspected that this fine material might exhibit different chemical properties than the coarser material. No corresponding control was processed.

All reactions were carried out in a Parr Instrument Company series 4052 pressure reaction apparatus. This instrument is equipped with a 300-ml capacity glass liner, which was used throughout the investigation.

Upon completion of the hydrogenation reaction, the bomb was allowed to cool to ambient temperature and opened. It was then reheated to about 85 C, and the hot contents were filtered to remove the catalyst and bark residue. The reheating step was required to resolubilize materials not soluble in dioxane-water at room temperature. The reaction mix was allowed to stand for several days at room temperature to permit insoluble condensation materials to form that were insoluble on reheating. After standing, the mixture was reheated, filtered, and made up to standard volume while hot. Aliquot portions of the hot mix were then vacuum distilled, with water additions, to remove dioxane. Once the dioxane had been removed, as indicated by the refractive index of the distillate, the water solubles and insolubles were separated by filtration. The water insolubles were washed with water, vacuum dried, and dissolved in ethanol.

RESULTS

Reaction conditions and residual hydrogen pressures are shown in Table 1 for the samples reacted. The control samples are not shown but were reacted under similar conditions. Samples reacting with hydrogen exhibited a definite exotherm beginning at about 231 C which was accompanied by a rapid temperature and pressure rise. At this point care in temperature control was essential to prevent temperatures from exceeding 250 C, which can lead to carbonization. The time temperatures exceeded 231 C was not held constant but purposely varied to assure that the sample was completely reacted and saturated with hydrogen. Hydrogen pressure, the most sensitive indicator of the progress of the reaction, is shown in Table 1 column 6, indicating that the reaction was complete within five to six hours with an average of 5.4 h. Column 9 in the table indicates that all samples consumed hydrogen, since ending pressures are all below the initial pressure of 68 atmospheres. It was very difficult to control accurately the input volumes of

TABLE 1. *Table of reaction conditions observed in hydrogenation experiments.*

Experiment number [1]	Order number 2	Bark M.C. % 3	Approximate solvent volume (ml) 4	Time temp. above 231 C heat on (h) 5	Time to constant pressure (h) 6	Maximum temp. observed (deg. C) 7	Maximum pressure observed (atmos.)[4] 8	Final pressure at R.T. (atmos.)[3,4] 9
EB 05	1	14.6	300 (B)	6.1	5.2	244	142.8	54.4(−)
WB 02	3	15.3	300 (B)	6.1	5.7	246	132.6	54.4(−)
WB 02A[2]	—	10.4	300 (NB)	9.4	5.8	245	136.0	51.0
EB 03	2	9.4	200 (NB)	7.1	5.9	242	139.4	54.4(−)
WB 01	8	9.7	200 (NB)	7.3	5.0	242	136.0	54.4(−)
WB 00	9	9.7	250 (NB)	10.2	5.4	241	129.2	51.0
EB 04	12	13.2	200 (NB)	6.8	4.6	241	136.0	51.0
WBF 01		9.9	200 (B)	6.2	5.4	237	136.0	54.4(−)

[1] EB—Substrate extracted bark, WB—substrate whole bark, WBF—substrate whole bark fines.
[2] A rerun of WB 02 in an attempt to increase recovery.
[3] Initial hydrogen pressure in all experiments was 68 atmos.
[4] Estimated to nearest 3.4 atmospheres since gauge calibrated in 100 psi increments.
(B) Blender used; (NB) No blender used.

bark, solvent, and catalyst; and any variations in input volumes make void volume calculations suspect. Without accurate void volumes, hydrogen consumption calculations are not valid, so these calculations were not attempted. Column 4, Table 1, indicates that a blender was employed with some reactions but not others. Because its use made it difficult to maintain a quantitative experiment and restrict solvent volumes to that of the glass liner, it was discontinued, with no apparent detriment to the completion of the reaction.

The results of the hydrogenation runs are shown in Table 2. The third column in the table indicates that 70–80% of the dry bark weight was lost by the test samples, with a loss of about 50–60% being noted for the controls. The most significant feature in the table is the increase in the percentage of the water-soluble fraction as compared to that of the controls: 32–35% versus 14–16% for the controls. The water-soluble fraction was successively extracted with ether and chloroform to give the values shown in columns 6 and 7 of the table. The alcohol-soluble fraction does not appear to be greatly influenced by the reaction except for the extracted bark samples, which when tested by the Wilcoxon Rank Sum Test, differed from the controls at the 95% level. On the basis of the tabular data, the WBF sample does not appear to differ chemically from the other reacted samples. The intent of the analysis shown in the table was to make it summative; however, as can be seen by the recovery percentages, the analysis did not meet this objective. The reacted samples, except for the WBF sample, show unaccounted-for losses of 24–25%, whereas the control samples and the WBF sample show losses of about 15–18%. The data in columns 4, 9, 10, and 11 were areas where losses might be expected. They were sampled to determine the magnitude and to improve the recovery. There could well be some loss due to the formation of noncondensable gases such as methane and ethane, which in combination with residual hydrogen are not easily quantified except by methods employed in stack gas analysis. The source of the greatest loss was from the reaction mix either boiling or sloshing out of the vent in the glass liner into the space between the liner and the steel bomb. When this occurred, and it always did, the material became baked on the outside of the liner and the rather rough walls of the bomb,

TABLE 2. *Average percent yield by fraction for hydrogenated and control bark samples based on ovendry weight of the respective bark samples.*

Treatment and substrate[1] 1	No. samp. 2	Unreacted bark residue 3	CHCl₃ sol. in residue 4	Water sol. ext.			Alc. sol. ext. 8	Residue soluble water wash[2] 9	Insol. formed react. mix[2] 10	CO₂[2] 11	Recovery[3] 12
				Total water sol. 5	Ether sol. 6	CHCl₃ sol. 7					
HEB	3	22.3	1.5	34.1	4.9	3.6	16.5	0.3 [2]	0.8	0.4 [1]	75.3
CEB	3	40.7	0.8	16.4	4.5	1.5	19.7	0.8 [2]	2.5	7.0 [2]	84.9
HWB	4	20.6	2.1	31.8	5.3	3.4	19.2	0.4 [2]	2.0	0.0 [1]	76.5
CWB	3	42.0	1.7	13.7	4.2	2.2	20.5	0.2 [2]	4.2 [2]	2.1 [1]	82.2
HWBF	1	24.0	2.8	34.8	—	—	21.8	0.4	0.6	0.1	84.6

[1] H—Hydrogenated, C—control, EB—extract bark, WB—whole bark, WBF—whole bark fines.
[2] Number in brackets immediately following number in table is number of observations if different from number of samples.
[3] Percentages not additive since data in columns 9, 10, 11 not common to all samples.

even though this space was partially filled with reaction solvent to help equalize vapor pressure inside and outside the liner.

Despite the use of different procedures for the dilute base extraction of the phenolic acids, all phenolic acid extracts remained unreactive when hydrogenated. Initially it was felt that the mode of extraction might be responsible for this lack of reactivity, which accounts for the investigation of the various extraction procedures. It was subsequently found that phenolic acid extracts became reactive when the catalyst to acceptor ratio was raised to 1:1. However, in-depth analysis of the reacted phenolic acids was not pursued.

FRACTION ANALYSIS — METHODS AND RESULTS

One of the objectives of this research was to separate the reaction products in sufficient quantities so that they could be identified using standard techniques of organic chemistry. Since the water-soluble fraction (WSF) was the fraction most affected by the reaction, separation of it into its components became a primary objective of the study.

With the exception of the gas-liquid chromatograph-mass spectrometer analysis discussed below, the chromatographic separations performed on the WSF were done with a Bendix Model 2300 temperature programmable, gas-liquid chromatograph (glc) having flame ionization detectors. The chromatograph was initially equipped with two 5-ft (1.524 m) × 0.125 in. (3.2 mm) OD columns packed with "Chromosorb W 60/80" support and "Carbowax 20M" as the stationary phase. Later similar columns having Free Fatty Acid Phase "FFAP" as the stationary phase were used.

Figure 1 shows the WSF of whole bark (WB) to be a mixture of some 20–30 compounds, with some peaks containing more than one component. Gas chromatographs of the WSF of extracted bark (EB) are quite similar to that shown in Fig. 1. Chemically the compounds in the WSF appear to be neutral or weakly acidic, largely insoluble in hydrocarbons such as petroleum ether or benzene, soluble in ethanol, dioxane, dioxane-water, and partially soluble in ether, chloroform, and the higher alcohols. They did not reduce Tollen's Reagent in ten minutes but with slight heating formed the classic silver mirror, indicating that the reductive component is either weak or present in low concentrations. The substances in this fraction do not lend themselves to standard separation techniques. Based on the chemistry of the fraction, one would suspect the presence of alcohols, diols, and related compounds although attempts at derivative formation were unsuccessful.

Gas chromatography followed by mass spectra analysis reinforced the contention that the compounds in the WSF were of the types mentioned. The mass spectra of the peaks from the glc were matched to spectra in a library of some 25,409 compounds, and the best matches plus the probability based on 1,000 that the unknown substance was the same as that in the library was computed. The results of this analysis in descending order of probability are as follows:

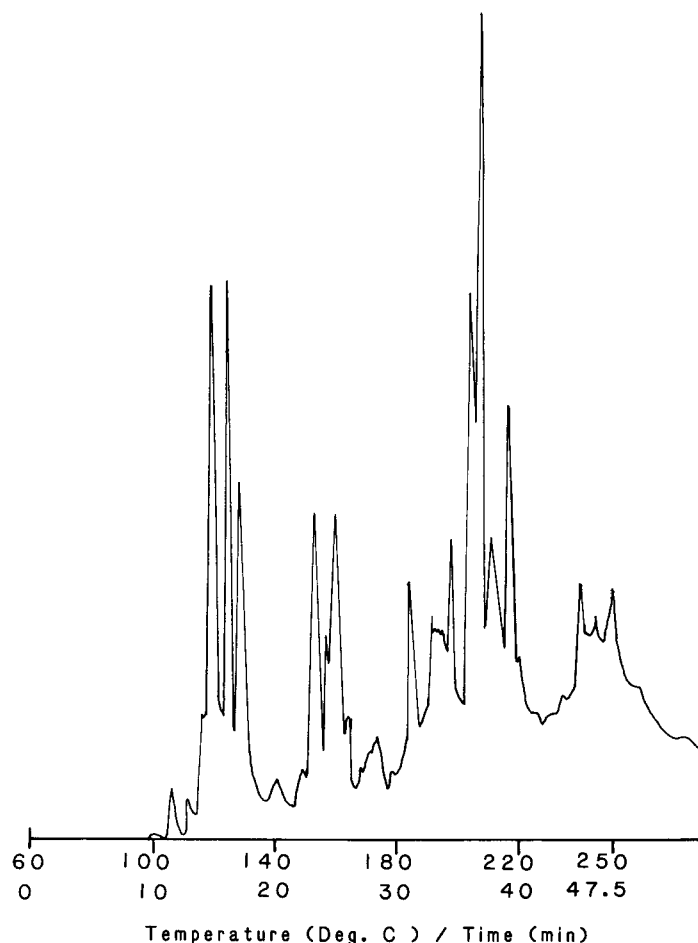| Compound	Probability
1,2-Cyclohexanediol	986
Same (isomer)	981
2,3-Butanediol	957
2,2'-Oxybis Ethanol	956

Temperature (Deg. C) / Time (min)

Fig. 1.   Gas chromatography of water-soluble fraction from whole bark sample WB 01. Conditions: 5' FFAP column, inlet 200 C, program 60–250 C at 4° per min, sensitivity 2000 k, recorder 0.1″/min, sample 3 microliters.

1,4-Butanediol	951
1-Methoxy-2-Butanol	928
1,2-Butanediol	924
1,3-Cyclohexanediol	900

On the basis of the probability assignments, it is likely that at least the first five substances were present in the fraction, and if not, the unknown compound would be structurally similar to that identified.

Column chromatography employing a techique for separating diols described by Dal Nogare (1953) was used in an attempt to separate the WSF into more discrete fractions. The procedure consists of separating the mixture on a silica gel-infusorial earth column, using a solvent gradient of butanol-chloroform and collecting the column effluent in 10-ml sequential increments. The samples are then reacted with sodium metaperiodate with excess periodate being back-titrated with sodium hydroxide. The sodium metaperiodate attacks vicinal (adjacent) OH
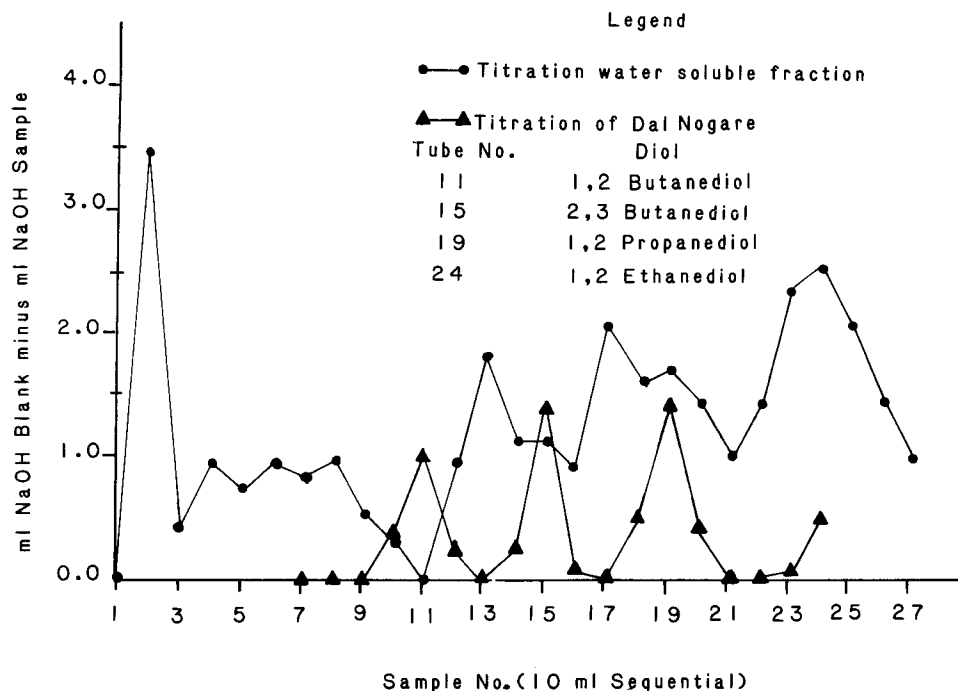
FIG. 2. Sodium hydroxide back titration of unreacted sodium meta periodate in sequential sample tubes from Dal Nogare column after solvent elution of the WSF. Demonstrates presence of vicinal OH groups. (Dal Nogare titration printed with permission of American Chemical Society.)

groups in the diols cleaving the C-C bond between them, yielding two aldehydes as reaction products. The results of a titration using the Dal Nogare procedure on the WSF appears in Fig. 2. A titration series conducted by Dal Nogare is superimposed for comparison. While the sample titration does not agree with the titration of known compounds; a shift of the sample peaks two tubes to the right makes the unknown series match the knowns quite closely. The results indicate the presence of vicinal OH groups since other data and tests did not indicate the presence of interfering compounds including carbohydrates. An attempt was made to improve separation by increasing column length as well as the amount of packing, which was increased by a factor of 1.5. Two of these larger columns were packed and the mixture was separated on them. The peaks of the larger columns differed markedly from those shown in Fig. 2. Gas chromatography of the peaks indicated that the peaks were still mixtures, though simpler than had been obtained previously. Additional refinement of the technique is required to improve component separation.

A nitration procedure followed by column chromatography was devised by Wekell et al. (1964) for the higher alcohols and diols. Nitration did not induce enough of a polarity differential to provide for separation using their chromatographic techniques. Combining the methods of Dal Nogare and Wekell et al. could produce better chromatographic resolution.

CONCLUSIONS

The data indicate that both whole and extracted bark are subject to hydrogenation and/or hydrogenolysis when exposed to the appropriate conditions of temperature, pressure, and a Raney-nickel catalyst to acceptor weight ratio of 0.75: 1. The reaction is completed after a period of about five hours at temperatures in excess of 231 C and an initial hydrogen pressure of 68 atmospheres. Temperatures in excess of 250 C promote carbonization and should be avoided.

Weight loss of extracted bark when exposed to the reaction was 77.7% of the dry bark weight, whereas the whole bark lost 79.4%. Based on the respective dry bark weight for the samples, the reacted extracted bark lost 18.4% more weight than did the controls, while the whole bark lost 21.4% more weight. The greatest chemical alteration occurs in the water-soluble fraction (WSF), where an increase of about 18% of the dry bark weight was noted for both extracted and whole bark over the respective controls. There is no apparent advantage to preextracting bark prior to the hydrogenation reaction.

The principal reaction products (WSF) formed by the hydrogenation of bark are not readily separable and remain mixtures even after being subjected to rather refined techniques. Those products that were tentatively separated and identified were the lower substituted alcohols, the lower alcohols, and vicinal and non-vicinal diols. None of the reaction products appear to occur in sufficiently large quantities to warrant separation. Few of the compounds have application as chemical feed stocks, though with modification some could be made useful such as converting cyclohexanediol to cyclohexanol. Use as fuel extenders or additives has yet to be explored.

Bark phenolic acids are resistant to high pressure hydrogenation regardless of the dilute base extraction procedure used. They can be made to react under the conditions employed if the catalyst to acceptor ratio is increased to 1:1. The products of the reaction were not investigated.

The reduction of bark via high pressure hydrogenation does not substantially simplify bark chemistry nor does it favor formation of any singular component or group of components. While not previously mentioned, a difficult to separate bark-catalyst complex was formed which would negate the use of the reaction even with valuable reaction products. The bark residue could only be separated from the Raney-nickel catalyst by dissolution of the catalyst with 10% HCl.

REFERENCES

DAL NOGARE, S. 1953. Chromatographic separation of glycols and monohydric alcohols. J. Am. Chem. Soc. 54(12):4116–4117.

FIESER, L. F., AND MARY FIESER. 1967. Reagents for organic synthesis. John Wiley and Sons, Inc., NY. 800 pp.

GEDNEY, D. R. 1971. Residues from primary manufacturing. Forest Ind. 98(12):24–25.

HALL, J. A. 1971. Bark—Old and new *in* Converting bark into opportunities. Proceedings of a conference held at Oregon State University. March 8–9. Compiled by A. C. VanVliet. Oregon State University, Corvallis, Oregon. 109 pp.

HARRIS, E. E., J. D'IANNI, AND H. B. ADKINS. 1938. Reaction of hardwood lignin with hydrogen. J. Am. Chem. Soc. 60(6):1467–1470.

HRUTFIORD, B. F. 1971. Reduction and hydrogenolysis. Pages 487–509 *in* K. V. Sarkanen and C. H. Ludwig, eds. Lignins, occurrence, formation, structure and reactions. Wiley-Interscience, NY.

MARTIN, R. E. 1969. Characteristics of southern pine barks. Forest Prod. J. 19(8):23–30.

McGinnis, G. D., and S. Parikh. 1975. The chemical constituents of loblolly pine bark. Wood Science 7(4):295–297.

Monzingo, R. 1955. Catalyst, Raney-nickel W-2. Pages 181–183 *in* E. C. Horning, ed. Organic synthesis collective, vol. 3. John Wiley and Sons, Inc., NY.

Nickles, W. C., and J. W. Rowe. 1962. Chemistry of western pine bark. Forest Prod. J. 12(8):374–376.

Pepper, J. M., and D. C. Hagerman. 1954. The isolation and oxidation of aspen lignin. Canadian J. Chem. 32:614–627.

————, and H. Hibbert. 1948. Studies on lignin and related compounds LXXXVII. High pressure hydrogenation of maple wood. J. Am. Chem. Soc. 70(1):67–71.

————, and W. Steck. 1963. The effect of time and temperature on the hydrogenation of aspen lignin. Canadian J. Chem. 41:2867–2875.

Ross, W. D. 1966. Bibliography of bark. Bibliographical Series 6. Forest Research Laboratory. Oregon State University, Corvallis, Oregon. 56 pp.

Sarles, R. 1973. Using and marketing bark residues. Forest Prod. J. 23(8):10–14.

Wekell, J. C., C. R. Houle, and D. C. Malins. 1964. A method for the isolation of mono- and di-hydric alcohols from complex mixtures. J. Chromatography 14:529–531.