ACID AND NEUTRAL SULFITE SEMICHEMICAL PULPING OF SIX ARKANSAS DELTA HARDWOODS

April 1942

No. 1292

UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison 5, Wisconsin
In Cooperation with the University of Wisconsin

ACID AND NEUTRAL SULFITE SEMICHEMICAL PULPING OF SIX ARKANSAS DELTA HARDWOODS

By

J. N. MCGOVERN, Assistant Technologist
and
G. H. CHIDESTER, Senior Engineer

Forest Products Laboratory,[1] Forest Service
U. S. Department of Agriculture

ABSTRACT

Semichemical pulping processes, using both acid and neutral sulfite liquors, were applied to the following six Arkansas Delta hardwoods: black willow, southern cottonwood, American elm, sugarberry, green ash, and bitter pecan. Pulping conditions for yields of 75 to 80 percent were determined and the properties of both the pulps and nine-point boards produced from them were evaluated. The general results were as follows: (1) Both the acid and neutral sulfite processes caused greater lignin removals from willow and cottonwood yet the pulps had lower lignin contents and higher alpha and total cellulose contents than did the pulps from the other woods. (2) The neutral sulfite pulps from willow, cottonwood, and sugarberry had strength properties superior to those of the pulps from the other woods. (3) The acid sulfite process caused greater removal of lignin and cellulose but less removal of material soluble in 1 percent caustic soda than did the neutral sulfite process. The pulps from the acid process had lower strength values than those from the neutral process. (4) The properties of nine-point corrugating boards made from the neutral sulfite pulps, especially those from willow, cottonwood, and sugarberry, were equal or superior to the properties of many commercial boards. (5) The nine-point boards made from acid sulfite pulps were inferior to those from the neutral sulfite pulps.

INTRODUCTION

A vital problem in forest utilization exists today in the productive use of the hardwoods which compose a predominant part of many of our forests. In the lower South, for example, 51 percent of the forest area is occupied by hardwood forest types and 63 percent of the total volume of usable wood is contained in hardwood trees, as revealed by the recent Federal Forest Survey (1). These figures make apparent the critical need for effective hardwood utilization in that region.

---

[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

A logical outlet for many of the hardwoods appears to be in the form of pulpwood, and the possibilities of hardwoods for pulping purposes have been recently outlined by the Forest Products Laboratory (2). The production of pulp from hardwoods is particularly significant at this time in view of the threatened shortage of wood pulp in the United States.

The Forest Products Laboratory has recently investigated the pulping of six species from Phillips County, Arkansas. This delta region supports almost pure stands of bottomland hardwoods. The species studied were black willow (Salix nigra), southern cottonwood (Populus deltoides virginiana), American elm (Ulmus americana), sugarberry (Celtis laevigata), green ash (Fraxinus pennsylvanica lanceolata), and bitter pecan (Hicoria texana). These representative species have been subjected to various pulping processes, including the acid and neutral sulfite semichemical pulping procedures with which this report is especially concerned. The neutral sulfite semichemical pulping, in particular, was applied to these woods because it had been previously found (1) that pulps prepared according to this process had promising outlets for news, board, and liner and, after further purification, for high-grade pulps.

The immediate objectives in the pulping of these woods by the acid and neutral sulfite semichemical procedures were (1) to establish suitable digestion conditions for yields in the range 75 to 80 percent and to evaluate the pulps so produced; (2) to produce pulps in semicommercial quantities for conversion into nine-point corrugating board and to evaluate the boards so produced; and (3) to compare the acid sulfite and the neutral sulfite semichemical pulps, and the nine-point boards made from both.

EXPERIMENTAL PART

For the pulping experiments each of the six hardwoods was converted into standard 5/8-inch chips. Preliminary trials to establish cooking conditions suitable for a yield from 75 to 80 percent were made in a 1.5 cubic-foot, alloy-clad, steam-jacketed autoclave. Larger-scale digestions to furnish material for nine-point boards were conducted in an alloy-lined, steam-jacketed, tumbling digester having a capacity of 13 cubic feet. The preliminary neutral sulfite digestions were designated as series I, the larger-scale neutral sulfite digestions as series II, the preliminary acid sulfite digestions as series III, and the larger-scale acid sulfite digestions as series IV.

The neutral sulfite liquors were prepared by dissolving sodium sulfite and sodium bicarbonate in water and diluting to the desired concentration. Fresh liquor was used for each of the digestions in series I, whereas in series II after the first digestion with fresh liquor the blow-back liquor from the previous digestion was utilized in making up the liquor for each succeeding digestion. The concentration of the neutral sulfite liquors was approximately 75 grams per liter of sodium sulfite and 15 grams per liter of sodium bicarbonate (calculated as the carbonate) for practically all digestions.

The acid sulfite liquors were prepared by passing sulfur dioxide from a cylinder into milk-of-lime. The concentration for all digestions was 6 percent total with 0.90 percent combined sulfur dioxide.

The digestions with the neutral sulfite liquor were carried out as follows: The chips in the autoclave or digester were steamed at atmospheric pressure for one-half hour. The impregnation liquor was then charged and the temperature raised by indirect and direct steam to approximately 120° C. The rise required 14 minutes in series I and 32 minutes in series II. The temperature was maintained at this level for from 45 to 60 minutes, during which time the pressure was held at 100 pounds per square inch by means of steam introduced at the top of the autoclave or digester. Upon completing the impregnation period, all excess liquor was blown from the digester and the temperature raised to approximately 170° C. by indirect and direct steam. The rise required 11 minutes in series I and 18 minutes in series II. The cooking period was continued for from 45 to 90 minutes at this temperature level, after which the steam was shut off and the pressure relieved. The chips were dumped from the digester and washed thoroughly with hot water. The chemical absorbed by the chips during the impregnation period was determined by the difference between the amount of chemical in the blowback solution and that in the initial liquor charged. The method of analyzing the liquors has been described previously (3).

The digestions with the acid sulfite liquor followed usual sulfite pulping procedure, except for a shortened cooking schedule. The temperature was raised to 110° C. in 2 hours, followed by a rise to 130° C. in 2 hours more. In the first trial digestion the temperature was held at 130° C. for 1 hour before starting the pressure relief; in all other digestions the pressure relief was started when the maximum temperature of 130° C. was reached in 4 hours. The pressure relief required 13 minutes in series III and from 45 to 60 minutes in series IV. The chips were removed from the autoclave or digester by dumping, after which they were washed with water.

The yields of the pulps were based in all instances on the moisture-free weights of the pulps defibered in a 5-pound beater. All the chips from the autoclave digesters were defibered in the beater, whereas only a sample of digested chips from the larger-scale digestions was thus defibered. The remaining chips from the larger-scale digestions were processed in a Bauer mill. Strength and chemical tests were made on the beater-defibered material in the case of the autoclave pulps and on the Bauer-milled material for the larger-scale pulps. The strength characteristics of the pulp were determined by test beater processing. The nine-point boards made from Bauer-milled pulps were also tested for strength and in addition the color was measured by the blue reading on an Ives photometer. All tests were made according to standard Forest Products Laboratory methods.

DISCUSSION

The Wood

The six hardwoods employed in these experiments had certain material differences in their physical and chemical properties. The data presented in table 1 were taken from a more complete report describing these woods (4). The most notable differences between the woods occurred in their densities and cellulose contents, which covered a considerable range.

The variation in density was perhaps the most pronounced of all the properties, the range being from 23 pounds for the comparatively light willow and cottonwood to 36 pounds per cubic foot for the relatively heavy pecan. The density was therefore considered the basic variable for purposes of later comparisons between the woods. While all the woods were classed as young and rapid growing, the willow and cottonwood were outstanding in this respect, being comparable to rapid-growth southern pine. The data in table 1 also indicated that some of the logs were larger in diameter than is common for pulpwood. It is interesting to note that the sugarberry and green ash contained no heartwood.

The total cellulose contents of the hardwoods differed to a considerable extent, varying from 54 percent for green ash to 63 percent for cottonwood. There was a trend toward increasing cellulose content with decreasing density. The three lightest woods had relatively high alpha cellulose contents in comparison with the three heaviest woods. Except for the low lignin content of the sugarberry, this component increased roughly with density. The pentosan contents showed no definite change from species to species, except that that of the sugarberry was somewhat higher than the others. With the exception of ether solubility, the ash and sugarberry had generally a higher solubility in the various solvents than the other woods. The material soluble in ether was low while that soluble in 1 percent caustic soda was relatively high for all species.

Neutral Sulfite Semichemical Pulping

Series I. Preliminary Autoclave Experiments

Several trials were necessary with sugarberry, the first wood tested, in order to establish impregnation and cooking conditions suitable for yields in the range of 75 to 80 percent. It was found that relatively moderate conditions produced a pulp having a yield in the desired range. Briefly, the general conditions found to be satisfactory were an impregnation at 120° C. for 45 minutes with a liquor containing 75 grams of sodium sulfite and 15 grams per liter of sodium bicarbonate (as the

carbonate) and a cooking period of 45 minutes at 170° C. These general conditions were applied to all the woods with two exceptions. In the case of the bitter pecan (No. 319, table 2) an increased impregnation time of 60 compared with 45 minutes was required for sufficient chemical absorption because of the relatively high density of this species. In the case of the American elm (No. 334, table 2) a cooking time of 60 instead of 45 minutes was needed for a yield in the desired range. There was no apparent reason why the lignin and hemicellulosic matter, the main constituents besides extractives removed during pulping, should be more difficult to remove from elm than the other species.

Certain differences in the absorption of chemical during impregnation and in the strength properties and chemical analyses of the pulps from the various woods were noted from the results of the digestions performed as described above. Some of these differences could be related to the physical and chemical characteristics of the woods themselves. The data are given in tables 2, 3, and 4. With impregnation conditions approximately the same for the six species, the volume of neutral sulfite liquor retained, and to a lesser extent the total chemical absorbed, decreased with an increase in wood density, as shown in table 2, series I. It is to be noted that, even with a slightly longer impregnation time, the least amount of chemical was absorbed by the most dense wood, bitter pecan, and yet a sufficient amount was present to bring about the desired pulping.

Except for a practically constant residual sulfite content in the spent liquor, all of the chemical absorbed during the impregnation period was consumed during the cooking stage, regardless of the amount initially present. The yields of defibered pulp from the six hardwoods fell in the relatively narrow range of 76 to 79 percent when the cooking conditions were closely alike, except for the differing amounts of chemical present at the start of cooking. It appeared, therefore, that only a certain minimum of chemical was needed to pulp these woods to a definite yield. The small yield variation also indicated that the sum of the lignin, cellulosic, and extractive material removed during cooking was approximately the same for all species. The percentages of each chemical constituent present in the different pulps and the percentages of the original constituents removed varied, however, with species, as shown in table 3, series I.

The chemical analyses of the pulps showed that their lignin contents fell in the same order as those of the respective woods, except for the sugarberry, whose pulp lignin content was high in relation to its wood lignin content. The percentage of the original lignin content removed from cottonwood and willow, however, was considerably higher than that from the other woods; approximately 50 for the former as compared to 30 for the latter. This higher percentage of lignin removed from cottonwood and willow would be important where subsequent purification to a more delignified pulp is desired.

As with the lignin, the total cellulose contents of the pulps fell roughly in the same order as those of the woods, again with the exception of the sugarberry, which had a pulp value higher than might be predicted on the

basis of the cellulose content of the wood. The willow and cottonwood pulps have outstandingly high cellulose contents compared with the others. The percentage of the original total cellulose removed varied between 2 and 6 percent, with no particular order in regard to other properties. This relatively low cellulose removal illustrated the mild action of the neutral sulfite liquor. Excluding the elm, the alpha cellulose values of the pulps had the same order as this constituent in the original woods. The alpha cellulose values were higher for the cottonwood and willow than for the others. The percentage of alpha cellulose material removed during cooking was below 1 percent, except for the elm and pecan, which had relatively high values of 6.6 and 4.0 percent, respectively. The pentosan values for the pulps from the different woods did not differ greatly, but the percentage of original pentosan material removed by cooking varied between 22 and 37 percent. The percentage removal of material soluble in 1 percent caustic soda, a measure of the hemicellulosic constituents removed during pulping, was high, running from approximately 60 for cottonwood to over 80 percent for green ash.

The varying distribution, with species, of the amounts of the chief constituents removed during pulping is illustrated in table 3, series I, under the heading, "Amounts Removed from 100 Pounds of Wood." Whereas the total removal of lignin and cellulosic material varied by less than 3 pounds (approximately the same variation as for yield of defibered material), the actual amounts removed varied from a low lignin and high hemicellulose removal in the case of sugarberry to a high lignin and low hemicellulose removal in the case of the cottonwood. In addition, the elm and pecan underwent a certain removal of material of the alpha cellulose type.

The strength properties of the neutral sulfite semichemical pulps, tabulated in table 4, series I, covered the range typical for this type of pulp. The bursting, tearing, and tensile strength values placed the pulps from the willow and cottonwood ahead of the others, those from the sugarberry intermediate, and those from the ash, pecan, and elm last. The last three also required longer beating times to attain a given freeness and had lower solid fraction values than the others.

Series II. Digester Experiments

Application of the neutral sulfite semichemical pulping conditions developed in series I to the larger-scale digestions in series II produced results closely paralleling those discussed in the foregoing paragraphs. The actual digestion conditions used for series II, however, differed in some respects from those used for series I. The conditions and results can be compared in tables 2, 3, and 4. The weight of wood in the digester charged to capacity was proportional, of course, to the density of the species. With proportionally larger wood charges in the larger-scale digestions as compared to the preliminary ones, the impregnation stages for the former were made with lower liquor-wood ratios and showed lower chemical absorptions. Nevertheless, sufficient chemical was present in all cases to perform the desired cooking. All of this chemical, except a small residue