

THE SODIUM XYLENESULFONATE
PULPING OF
NORTHERN BLACK COTTONWOOD

by

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THE SODIUM XYLENESULFONATE
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I. INTRODUCTION

Wood, the principal raw material for paper making pulps, is composed of a cellulosic portion and a non-cellulosic portion. The non-cellulosic portion consists chiefly of lignin and the removal of this component from wood is the primary objective of all pulping processes. The principal pulping processes in use today accomplish the removal of lignin from wood by its reaction with some chemical present in the cooking liquor to form soluble lignin compounds.

In the alkaline cooking processes, soluble alkali-lignins are formed which are removed with the liquor leaving a product consisting of relatively pure cellulose. The lignin, comprising a large portion of the original wood, is not recovered as such. In those processes where chemical recovery is practiced, the lignin containing liquors are burned and from this combustion, the calorific value of the lignin is utilized, although the lignin itself is not. In a very limited number of operations, the lignin is recovered, but this recovery represents only a very small percentage of the total annual loss.

Soluble lignin-chlorides are formed by the action of chlorine on lignin-containing cellulosic materials.

These processes involve the loss of both lignin and cooking chemical, since up to the present time, no economical method for recovery of either has been proposed.

The sulfite process removes lignin from wood by the action of bisulfites forming salts of the sulfonated lignin which are soluble at the temperatures employed. Here again, no economical process is in general wide spread use at present whereby the lignin or the chemical is recovered. It is in this field, however, that the greatest amount of research and developement is being carried out. A number of processes have been proposed and a few experimental operations are being carried out, but no sound economical plan has yet been accepted.

In 1943, Ralph H. McKee of Columbia University was issued a patent for a fundamentally new pulping process involving the use of hydrotropic salts (5,p.1-6). This process was new in two important respects; (1) it provided for recovery of the cooking chemical as well as both the lignin and the cellulose, and (2) it did not involve reaction of a chemical in the cooking liquor with the lignin in cellulosic materials to form soluble compounds. The action of solutions of salts of aryl and arylsulfonic acids on lignin-containing cellulosic materials such as wood, flax straw, wheat straw, jute, bagasse, and similar materials was investigated. The cooking liquors used were solutions

of alkali salts of benzoic, salicylic, xylenesulfonic, cymenesulfonic, benzenesulfonic, phenolsulfonic, and toluenesulfonic acids.

These solutions are hydrotropic in that they have the property of "salting in" or increasing the solubility of many sparingly soluble organic and inorganic compounds in aqueous systems. No chemical reaction occurs between the lignin and the cooking chemical, therefore the lignin that is recovered closely resembles the lignin as it is found in wood. At the same time, the chemical in the waste liquor can easily be recovered for reuse by a comparatively simple process.

The cooking solutions used in McKee's process are reused several times before lignin is recovered, due to the increased effectiveness of the solvent as the lignin concentration therein increases. This increase in effectiveness continues until the solution becomes nearly saturated with lignin. In practice, this allows five to seven cooks using the same liquor. The lignin is then precipitated from solution by dilution with water and recovered by filtration. The liquor containing a dilute solution of the hydrotropic salt plus a small amount of impurities may then be evaporated back to the original concentration and used again. This process may be repeated until the concentration of the impurities (mostly silica, iron compounds, and

some organic acids) reaches a point where further use of the liquor without purification is undesirable. Purification may be simply carried out by adding lime to the liquor, filtering off the precipitated impurities, and re-concentrating the purified liquor to the desired concentration.

On his work using poplar wood, McKee reported total yields of 83 per cent of the oven-dry weight of the wood. The cellulose yield was reported as 53 per cent of the weight of oven-dry wood and the lignin, 30 per cent of the oven-dry weight. The quality of both products produced by this process was claimed to be much superior to that of similar products produced by present commercial processes. However, few types of wood were tried and little data on the results obtained are available.

McClintock, in his work on the assembly and trial operation of an experimental digester at Oregon State College in 1948, made several superficial cooking attempts using McKee's process (4,p.74-98). The wood used in these attempts was western hemlock (Tsuga heterophylla (Rafinesque) Sargent). Only visual evaluation of the pulp produced was undertaken and no analytical data on the products he obtained are available. A moderate degree of success was reported, and the suggestion was made that further work using the hydrotropic solutions as pulping agents be carried out.

II. STATEMENT OF THE PROBLEM

The advantages of a pulping process making use of a hydrotropic solution as a pulping agent are many. A few of these are:

1. A greater use may be made of the nation's forest resources. At the present time, scarcely 50 per cent of the wood consumed by the pulp industry is present in the final finished products. Lignin, if it were recovered, would add another 20 to 30 per cent to the wood utilized to produce salable products.
2. Another product, lignin, would improve the economics of the pulp industry if a reasonable process for its recovery were available. This process would make such recovery possible. Lignin, produced as a by-product of cellulose pulps, has already been found useful in many products and might conceivably someday be an important source of aromatic compounds.
3. The alleviation of the stream pollution problem that now exists would be an important point in favor of the adoption of such a process. Not only would the recreational use of our rivers be enhanced, but the fishing industry would benefit appreciably.

4. The absence of the objectionable fumes now produced by other processes makes this process highly desirable from the standpoint of public relations. Moreover, the carbon dioxide produced in this process is recoverable and could add still another salable by-product to the production of cellulose pulps.
5. Due to the simplicity of the liquor preparation, lignin recovery, chemical recovery, and liquor purification processes, equipment costs would be greatly reduced.
6. High initial cost of chemical is compensated by good recovery. Simplicity of operations in the recovery and purification process would keep mechanical losses low.

With these factors in mind, an investigation was planned to determine whether a common, commercially used wood could be successfully pulped by the hydrotropic solution process using sodium xylenesulfonate as the pulping chemical. An attempt was made to find conditions commercially feasible, that would produce products of satisfactory quality and quantity.

III. EXPERIMENTAL PROCEDURE

WOOD. The selection of northern black cottonwood (Populus trichocarpa hastata Henry) as the wood to be used in the pulping experiments was based on McKee's results showing greater success using deciduous woods, the relatively low lignin and extractive content of the wood, and on its availability in the immediate area.

Cottonwood is found in pure stands or groups, or in mixture with Douglas fir, lowland white fir, and red alder (3,p.86-87). Stands range from northern Alaska to northern California, eastward in Washington and Oregon to northwestern Montana, then north in the Rockies to the Yukon territory. The tree grows to a maximum of 175 to 225 feet in height and 7 to 8 feet in diameter in western Washington. The forest trees have a long, clear bole, lending themselves well to present type logging and chip producing techniques. The present utilization in the Northwest is chiefly in lumber for the manufacture of plywood, matches, and boxes, soda pulp, and the manufacture of excelsior. The supply amounts to 225 million cubic feet in the United States (1939).

The chips used in these pulping experiments were commercially produced and ranged in size from 1/2 to 1 1/2 inches in length. Approximately 200 pounds of moist chips

were donated by the Crown Zellerbach Corporation for these experiments. They were spread out on large trays, allowed to air dry, and then stored in burlap sacks until used.

COOKING LIQUOR. Two hundred pounds of technical grade sodium xylenesulfonate were donated by the Wyandotte Chemicals Company. The information on the product supplied by the manufacturer indicated that it was primarily composed of the sodium sulfonate derivatives of the 1,3-isomer with much smaller amounts of the 1,2-isomer. The product contains less than two per cent inorganic salts.

A 40 per cent (by weight) solution of this chemical was prepared by dissolving 100 pounds of the solid in 18 gallons of cold water. The resulting solution was straw colored, had a faint sweet odor, a pH of 8.8, and a specific gravity of 1.165 at 60°F.

Fresh cooking liquor was used in the first three cooks and the used liquor obtained from these cooks in the last two.

APPARATUS. The digester in which the cooking was carried out was a one cubic foot, stainless steel, stationary digester equipped with external electrical heating and arranged for "Mortrud" type circulation. No provision was made in the construction of this digester for blowing of the contents at the conclusion of a cook, therefore, the

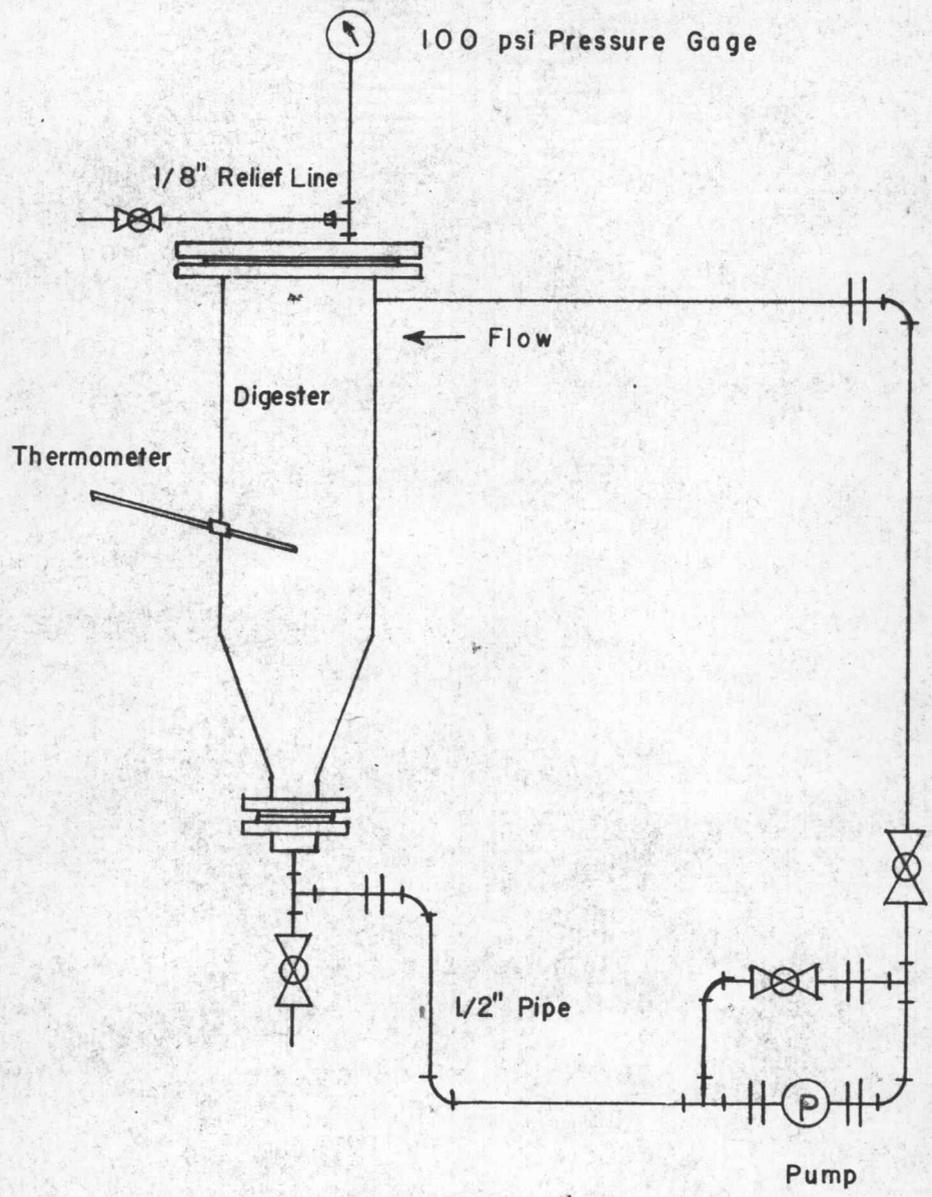


Figure 1. EXPERIMENTAL DIGESTER

SCALE: 1" = 1 Ft.

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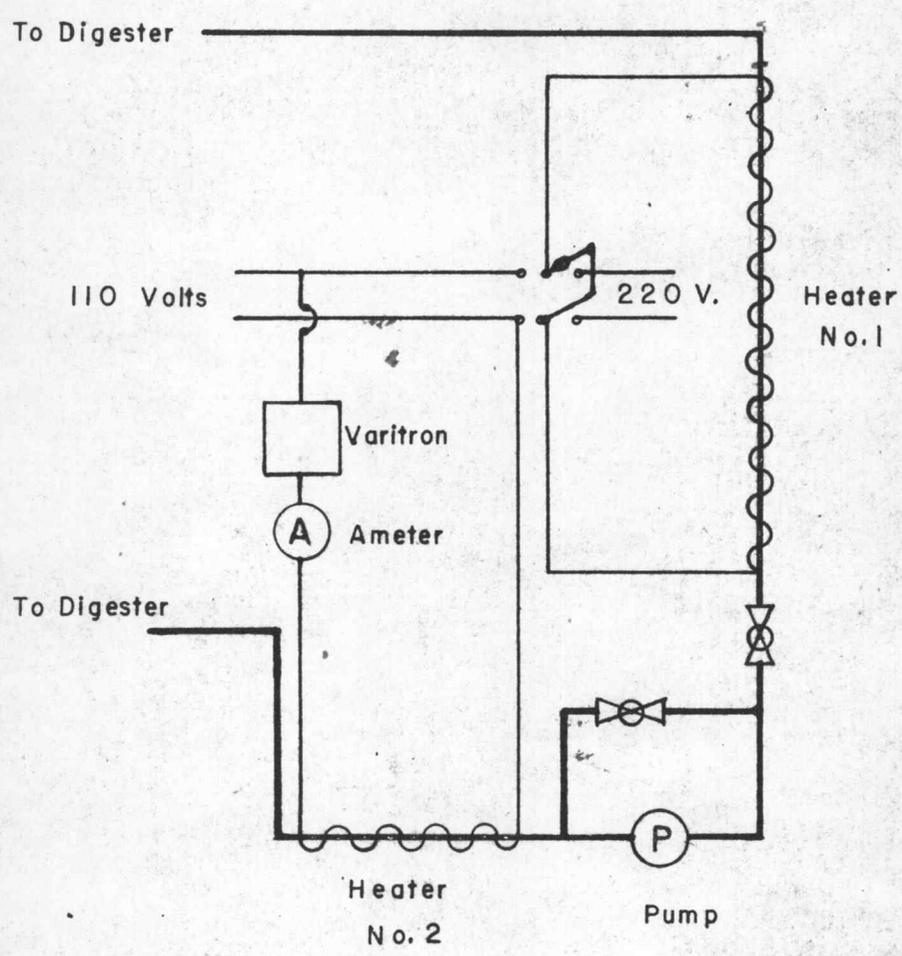


Figure 2. HEATER WIRING DIAGRAM

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chips were defibered after cooking by means of a Bauer Pulper. A diagram of the digester and its auxiliary equipment is shown in Illustration 1, and the heater wiring diagram is shown in Illustration 2. For details of digester construction, etc., reference may be made to McClintock's thesis (4,p.6 thru 47).

PULPING VARIABLES. The following is a list of the pulping variables that were considered.

1. The species of the wood.
2. The concentration of the cooking liquor.
3. The liquor to chip ratio.
4. The circulation rate of the cooking liquor.
5. The pH of the cooking liquor.
6. Reuse of the cooking liquor.
7. The operating temperature.
8. The operating pressure.
9. The cooking cycle.

Certain of these variables were kept constant while others were varied in the several cooks in order to determine the best possible cooking conditions.

The species of wood used was limited to northern black cottonwood. The reasons for this particular choice have already been presented.

The concentration of the cooking liquor was chosen as 40 per cent on the basis of previous work by McKee and McClintock as well as the fact that although higher concentrations might be desirable in producing greater hydro-tropic effects they would be economically unfeasible and commercially difficult to handle.

The ratio of liquor to chips was partially determined by the spacial limitations of the digester itself. The procedure used in filling the digester was to fill it to a reasonable depth with air-dry chips, placing large chips directly over the bottom screen to prevent plugging, and filling with hot (200°F.) liquor. The ratio was kept below ten to one, although it was felt that any ratio used in this experimental work would not be directly applicable to large size commercial operations. Lower ratios could, no doubt, be used in a commercial scale cooking process with the same results.

The circulation rate of the liquor was fixed by the maximum capacity of the pump. Operation with the pump bypass open even slightly was not considered feasible due to resultant over heating of the liquor in the heating leg at low liquor velocities.

No attempt was made to alter the pH of the cooking liquor in any way.

Reuse of the cooking liquor was utilized in the last two cooks to determine whether the hydrotropic effect was greater than when using fresh liquor. However, it was kept in mind, that cooking conditions producing satisfactory results with fresh liquor must be found, as fresh liquor would have to be used at some time in any commercial operation.

The initial operating temperature was chosen as 300°F. on the basis of previous work. This was raised to 325°F. in the fifth cook.

The operating pressure was maintained at a value corresponding to the temperature, or as nearly that as possible. Considerable difficulty was encountered during the several cooks in maintaining a relatively constant temperature and pressure. This was believed due to the high heat capacity of the digester and contents and the low liquor circulation velocity. Over heating seemed to take place in the vicinity of the heating coils causing the liquor to vaporize. This raised the pressure greatly but had little effect on the temperature of the digester contents.

The cooking cycle was originally set at 12 hours overall; 2.5 hours to pressure, 9 hours at pressure, and 0.5 hour gassing down. This schedule was followed on cook number one resulting in apparently good penetration of

liquor into the chips as even the knots were softened considerably. In order to reduce the time spent in the laboratory, all other cooks were run on an 8 hour schedule with apparently as good results. Two and one half hours to pressure and one half hour gassing down were utilized as before.

COOKING. The purpose of the trial run was to become familiar with the digester operation and to test the circulation pump and heaters. Information was desired also on the initial rate of temperature rise and on the use of the various heating circuits to maintain a uniform temperature and pressure. In this trial run, no chips were used and the digester was filled with water. Total operating time was three hours. Approximately two and one half hours was found to be the time required for the temperature to rise to 300°F. starting with hot water. Data taken during the run may be found in the appendix, Table 5.

Cook No. 1. The digester was charged with 9 pounds of air-dry wood chips, 100 grams of which were removed for a moisture determination. Several handfuls of the larger chips were placed directly over the bottom screen plate to prevent plugging and resulting poor liquor circulation. The moisture determination in this and all subsequent cooks was carried out using the toluene distillation method.

Approximately six gallons of fresh liquor were heated to 200°F. and exactly six gallons of the hot liquor added to the chips in the digester. The cover was bolted down, the heater turned on connected to the 220 volt circuit, and the circulation pump started. Data recorded are found in the appendix, Table 6.

Regulation of the temperature was accomplished by turning the heater off as soon as the desired cooking temperature was attained and turning it back on for a few minutes, using the 110 volt circuit, when the temperature had dropped several degrees. Pressure was maintained at a corresponding value by applying intermittent relief.

At the completion of the cook, the spent liquor was drained and the chips washed in the digester first with fresh liquor and then with water. The chips were then removed from the digester, placed in a screen-bottomed box and thoroughly washed with water. The chips appeared dark brown in color and very soft; even those chips containing knots showing signs of good penetration. A moisture determination was made on a sample of the weighed wet chips using the xylene distillation method.

These chips were then run through a Bauer Pulper at a five mil plate setting, using cold water showers. A very low power consumption was required. An extremely slow,

fine, light-colored slush pulp was produced. This was then centrifuged and a portion broken up into small crumbs and allowed to air-dry. This portion was retained for analysis.

Cook No. 2. The same procedure was followed as in the first cook. The only condition changed was the duration of the cook, which was reduced from 12 hours to 8 hours. Data may be found in the appendix, Table 7.

The cooked chips were washed with 3 gallons of fresh liquor instead of 2, before washing with water. In order to produce a freer pulp, the Bauer plate setting was increased from 5 to 10 mils. The power required to defiber the chips from this cook was even less than in cook one. A somewhat freer pulp was produced.

Cook No. 3. No conditions were changed in the cooking procedure. However, the cooked chips were first allowed to soak overnight in 4 gallons of fresh 20 per cent liquor before washing with water. A sample of chips obtained before washing with water was kept for analysis as well as the usual sample from the air-dry, Bauer defibered pulp. The sample not washed with water was then defibered in the 20 per cent liquor by means of a Waring blender, washed thoroughly with water in a Buchner funnel, and air-dried. Data for this cook appear in the appendix, Table 8.

Cook No. 4. In this cook, 6 gallons of used liquor obtained from the three previous cooks were used rather

than fresh liquor. All other cooking conditions and procedure used were the same as before.

The cooked chips were allowed to soak overnight in the 20 per cent liquor obtained from cook three, then washed with water, passed thru the Bauer, centrifuged, and air-dried. A sample of the air-dry pulp was kept for analysis. Data appear in the appendix, Table 9.

Cook No. 5. The temperature, pressure, and liquor to wood ratio in this cook were increased. Used liquor from the first three cooks was again used as in cook four.

The cooked chips were washed directly with water and then allowed to soak overnight in water. The Bauer plate setting was increased from 10 to 20 mils. See the appendix, Table 10, for all data.

ANALYSIS OF ORIGINAL WOOD. It was necessary to carry out an analysis of the wood chips, placing primary emphasis on the lignin and holocellulose content, so that a comparison could be made with the analysis of the pulp produced and thereby determine the effectiveness of the pulping operations in removing lignin. As standard methods of analysis were used, it was first necessary to reduce a portion of the chips to wood meal.

This was accomplished by taking two samples from each bag of chips, one at the top and one about one half

of the way down in each bag. These samples were then combined and broken by hand into chips of uniform width (1/4 inch). These small chips were then passed through a Wiley mill and screened. The portion of the wood meal that passed through a U.S. standard 40 mesh screen was collected and placed in two large, glass, screw-top bottles. These were allowed to stand for several weeks, shaking them periodically, to allow moisture equilibrium to occur.

One portion of the prepared wood meal was used to prepare extractive free wood. The sample was extracted for 4 hours in a Soxhlet extractor with 1 to 2 alcohol-benzene solution. The wood meal was then filtered on a Buchner funnel and washed with 95 per cent ethyl alcohol to remove the benzene. This was followed by 4 hours of extraction with 95 per cent ethyl alcohol, air drying to remove the alcohol, and then 3 one-hour extractions with water at 100°C. The extractive free wood meal was allowed to air-dry and returned to the glass bottle until needed for analysis.

The moisture content of the unextracted and extractive-free wood meal was determined once, before any analyses were carried out. The values obtained were used in all subsequent calculations. The hot water, alcohol-benzene, and 1 per cent sodium hydroxide solubilities of the unextracted wood were then determined.

The lignin and chlorite holocellulose contents of the extractive-free wood were determined. All analyses were run at least in duplicate and all values reported are average values. No lignin determinations were carried out on the chlorite holocellulose, as comparative values only were desired.

ANALYSIS OF PULP. In all cases, the material to be analyzed was the air-dry product of the cooking, washing, and de-fibering operations. A suitable method of analysis had to be devised so that lignin and holocellulose contents of the pulps could be compared with those of the original wood.

For the pulps obtained in cooks one and two, lignin and holocellulose determinations were carried out directly on the air-dry pulp. This procedure was found to be unsatisfactory. The lignin that was isolated was more than 21 per cent soluble in alcohol-benzene solution before oven drying at 105°C., but only 2 per cent soluble after oven drying. This was an indication that something else besides lignin was being determined as lignin, probably some of the nonvolatile ether soluble extractives (resin and fatty acids, fats, phytosterols, waxes, and resenes) and the alcohol soluble extractives (coloring matter, tannins, phlobaphenes, lignans) that were originally present in the wood.

In all subsequent analyses, the air-dry pulp was first subjected to 4 hours extraction with alcohol-benzene solution. The per cent of extract in the pulp also served as an indication of the effectiveness of the washing operation. Holocellulose and lignin determinations were then carried out on the extracted pulp. This procedure proved to be very satisfactory. Permanganate number determinations were made on unextracted samples of all pulps obtained.

WASHING OF PULP. The procedure used to wash the chips after the cooking operation had considerable effect on the amount of organic material remaining in the pulp. The chips from cook three were divided into two portions; one was washed with and defibered in 20 per cent fresh cooking liquor (pulp 3A) and the other washed with 20 per cent fresh cooking liquor, then washed and defibered in water (pulp 3B). The latter procedure was found to result in less retention of alcohol-benzene soluble material in the pulp than the former.

Excessively high retention was found to occur when no liquor was used for a preliminary washing, and the chips were washed only with water before and after defibering. The lowest retention was observed when the chips were soaked overnight in 20 per cent used liquor, then washed

with water before defibering, and the pulp washed again with water in the centrifuge after defibering.

PRESSED BOARD. In order to determine to what uses a high lignin pulp, such as was produced by this process, might be put, a sample of pressed board was produced.

A mat of fibers one foot square and approximately 3/4 inch thick was made from the pulp obtained in cook number 4. This was faced on one side with a greased, stainless-steel platen and on the other side with a wire-mesh mat to allow easy escape of entrained water, and placed in a steam-heated, hydraulic press. The temperature of the press was 370°F. The following pressure schedule was followed:

500 p.s.i.g. for 5 sec. - falling gradually to-
100 p.s.i.g. in 15 sec. - held at-
100 p.s.i.g. for 2 min. - then raised to-
200 p.s.i.g. for 9 min.

A hard, smooth-surfaced board, light brown in color was produced. Samples of the finished board were cut out for physical tests which were run by members of the Oregon Forest Products Laboratory staff.

METHODS OF ANALYSIS. The following is a list of the methods used for the various analyses.

Wood meal		
T.A.P.P.I. Tentative Standard	T 11 m	(6)
Extractive-free wood		
T.A.P.P.I. Tentative Standard	T 12 m	(6)
Moisture in wood chips		
T.A.P.P.I. Standard Method	T 3 m 44	(6)
Alcohol-benzene solubility of wood		
T.A.P.P.I. Standard Method	T 6 m 45	(6)
1% NaOH solubility of wood		
T.A.P.P.I. Standard Method	T 4 m 44	(6)
Lignin in wood		
T.A.P.P.I. Standard Method	T 13 m 45	(6)
Lignin in pulp		
I.P.C. Standard Method		428 (2)
Hot water solubility of wood		
I.P.C. Standard Method		10 (2)
Chlorite holocellulose		
I.P.C. Standard Method		28 (2)
Moisture in wood meal and pulp		
I.P.C. Standard Method		3 (2)
Permanganate number of pulp		
I.P.C. Standard Method		410 (2)

IV. EXPERIMENTAL RESULTS

The results of the analysis of the original wood are given in Table 1 below. The value obtained for the 1 per cent sodium hydroxide solubility test indicates that the wood was not excessively rotted. The low lignin content of the wood also bears this out. The solubility determinations show that little extractive material is present in the original wood and any pulping action (i.e. loss in weight during cook) involves primarily the lignin and the holocellulose. All values given are per cent of oven-dry, unextracted wood.

TABLE 1.

Analysis of Northern Black Cottonwood

Hot water soluble	2.75%
Alcohol-benzene soluble	2.45%
1% NaOH soluble	18.1 %
Chlorite holocellulose	74.5 %
Lignin	<u>20.7 %</u>
Total	100.5 %

The results of the physical tests on the board samples submitted to the Oregon Forest Products Laboratory

for testing are given in Table 2. The per cent swelling, per cent moisture absorption, and modulus of rupture are of primary interest.

The per cent swelling was obtained by measuring the dimensions of a board sample before and after immersion in water at room temperature for 24 hours, and the per cent moisture absorption represents the corresponding increase in weight of the same sample. The values obtained were considered quite satisfactory considering the fact that no sizing or additives were combined with the pulp in the board. The addition of a small amount of size would have greatly reduced the moisture absorption and swelling but would have reduced the strength at the same time.

The modulus of rupture was measured using a 6 inch span and a headspeed of 2 inches per minute, on a 3 inch strip of board. A maximum load of 31 pounds was applied. The value obtained, 4620 pounds per square inch, is comparable to similar commercial products. However, the addition of a small amount of a phenolic resin or similar material, would greatly increase the strength of this board. As only one sample was tested, the values obtained for the various properties of the board are not truly representative values.

TABLE 2.

Physical Properties of Pressed Board

Thickness	0.144 inch
Density	56.0 lbs/ft ³
Specific gravity	0.90
Per cent swelling	23.6%
Per cent moisture absorption	63.9%
Modulus of rupture	4620 lbs/in ²

Table 3 below gives the results of the analyses carried out on the six pulps produced. All values are reported as per cent of the oven-dry, unextracted pulp.

The results of analyses on pulps produced in cooks number 1 and 2 were not very reliable due to the fact that no preliminary alcohol-benzene extractions were carried out. However, they served as samples on which a suitable analytical procedure was developed. The various values for each individual pulp did not total exactly 100 per cent as the holocellulose determinations were not corrected for residual lignin content.

The amount of alcohol-benzene soluble material remaining in the pulp was, in general, greater than that present in the original wood. Further examination of the

data also showed that the sum of the alcohol-benzene solubles plus lignin was greater in the pulp than in the original wood. These results indicated that in addition to the non-volatile, water insoluble extractives and precipitated lignin probably present in the pulp, some lignin-like, alcohol-benzene soluble material was produced in the cooking process and precipitated in the washing operation. The formation of such a material might possibly have occurred in the following way.

The removal of the lignin from wood in this process is probably accompanied by removal of a portion of the hemicelluloses (7,p.224). The subsequent hydrolysis of these hemicelluloses to produce pentose sugars would occur under the conditions of the cooking procedure. It has been shown (7,p.770-774) that treatment of wood with neutral salt solutions has a strong hydrolytic effect on the pentosans. Also, neutral salt cooking of Aspen (*Populus tremuloides*) yields material with an alcohol-benzene soluble fraction of the same order of magnitude as was found in this investigation (7,p.773 and 1,p.413-419).

A possible reaction by which pentoses can combine to form dihydroxycinnamic alcohol has been proposed by Klason (7,p.274). This material is capable of further polymerization to form lignin-like compounds. The formation of carbon dioxide in the cooking process is offered as supporting evidence for the proposed reaction.

The rather high lignin contents of the pulps was believed to be at least partially due to lignin actually removed by the cooking process but precipitated in the chips in the washing operation. This would also explain the high yields of pulp obtained. The effect of the washing procedure on the alcohol-benzene soluble portion of the pulp was quite noticeable on pulp 5, on which no liquor was used in the washing. The low alcohol-benzene soluble contents of pulps 3B and 4 indicated that a soaking in dilute liquor is desirable before washing.

TABLE 3.
Analysis of Pulps

Pulp No.	Alc-Benz Soluble	Lignin	Holo-cellulose	Total
1	not done	18.9	85.5	104.4
2	not done	12.1	78.2	90.3
3A	6.7	17.8	81.5	106.0
3B	2.2	14.3	83.0	99.5
4	3.9	17.9	82.1	103.9
5	8.0	7.7	86.6	102.3

Table 4 presents, in tabulated form, the values of various cooking variables and results for each cook carried

out. The values for the per cent lignin removed were calculated on the basis of the per cent lignin in the original wood, per cent cooking yield, and per cent lignin in the pulp produced. The permanganate numbers did not seem to be reliable indications of the extent of lignin removal, as they varied little throughout the several cooks. They are of importance, however, in that they were run on unextracted pulps and therefore indicate the amount of bleaching that would be necessary on these particular pulps as they would be produced in industry. All permanganate number determinations were carried out using 40 ml. of 0.1 N potassium permanganate solution. The values listed for alcohol-benzene solubility of the pulps were calculated on the basis of the oven-dry, unextracted pulp.

Key to Table 4

- A - cook number
- B - specific gravity of liquor before cook
- C - specific gravity of liquor after cook
- D - length of cook (hours)
- E - pH of liquor before cook
- F - pH of liquor after cook
- G - per cent yield
- H - first wash treatment
- I - second wash treatment

Key to Table 4
(continued)

- J - Bauer plate setting (mils)
- K - liquor to wood ratio
- L - cook temperature ($^{\circ}\text{F.}$)
- M - cook pressure (p.s.i.g.)
- N - permanganate number of pulp
- O - per cent alcohol-benzene soluble
- P - per cent lignin removal

TABLE 4

Cooking Conditions and Pulp Treatment

A*	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
1	1.165	1.190	12	8.8	4.1	----	fresh 40%	water	5	7.06	300	50	38.3	---	16.0
2	1.165	1.195	8	8.7	4.2	----	fresh 40%	water	10	7.06	300	50	38.0	---	----
3A	1.165	1.190	8	8.2	4.6	90.0	fresh 20%	fresh 20%	--	7.32	300	50	26.4	6.7	----
3B	1.165	1.190	8	8.2	4.6	90.0	fresh 20%	water	10	7.32	300	50	26.6	2.2	24.8
4	1.182	1.212	8	5.2	4.5	89.5	used 20%	water	10	7.15	300	50	26.0	3.9	23.6
5	1.182	1.206	8	5.2	---	80.5	water	water	20	9.16	325	90	26.1	8.0	72.0

*See explanation p. 28.

V. CONCLUSIONS

Under the experimental conditions that were tried, a satisfactory yield of pulp having a reasonably low lignin content was produced. A pulp having such properties, although by no means first grade material, could certainly find limited use, especially since recovery of the lignin and the pulping chemical are possible.

The results obtained in this investigation indicate that a further increase in temperature (above 325°F.) and a liquor to wood ratio in the neighborhood of 10 to 1 would produce a pulp of still lower lignin content. Further work using other species of hardwoods and possibly some softwoods seems desirable. The results obtained using a softwood having low pentosan content such as Douglas fir would provide information either in support of or against the proposed formation of lignin-like compounds.

The use of a satisfactory chip washing procedure appears of major importance in producing a satisfactory pulp. Commercially, however, the contents of the digester could be blown and the resultant defibered pulp allowed to soak in liquor followed by a counter-current washing operation using liquor in the initial wash and pure water in the final wash. It is believed that this type of washing would reduce the possibility of precipitating the dissolved lignin back onto the pulp.

The board produced was of comparable quality to commercial products in which no sizing or additives were used. The swelling and moisture absorption, although high, could be greatly reduced by the addition of a small amount of size. The strength, and also to a lesser extent the swelling and moisture absorption, could be improved by adding a resin or oil binder to the pulp.

Were further work carried out on this process and reasonable yields of lower lignin content pulp produced, bleaching studies on these pulps would be of considerable interest and importance. Also, a complete and detailed economic analysis of the process would be necessary in determining the feasibility of the commercial application of this process.

VI. SUMMARY

A set of pulping conditions, applicable to McKee's hydrotropic solution method, using sodium xylenesulfonate as the pulping chemical on northern black cottonwood, was sought that would produce a pulp of relatively low lignin content and in sufficient yield to be economically feasible.

The apparatus, operating procedure and methods of analysis used, as well as the results obtained are given. The physical properties of a pressed board made from one of the pulps obtained are presented.

Using an 8 hour cooking schedule, 40 per cent solution of sodium xylenesulfonate, liquor to wood ratio of 9.16 to 1, and cooking at pH 5.2-4.5 at 325°F., a 72 per cent lignin removal was obtained with an overall yield of 80.5 per cent.

A theory is proposed to explain the presence of lignin-like material in the pulp and presumably formed in some way as a result of the cooking process.

The significance of being able to produce a pulp containing in the neighborhood of 5 per cent lignin by this method as well as a suggestion for further work is given.

VII. BIBLIOGRAPHY

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VIII. APPENDIX

Data From Experimental Cooks

TABLE 5

Trial Run - July 6, 1950.

Chips: none

Liquor: water

<u>Time</u>	<u>T(°F.)</u>	<u>P(psig)</u>	<u>Remarks</u>
1425	175	0	Turned on pump, unit 1 on 220 v.
1500	206	2	----
1530	234	11	----
1600	258	23	----
1630	278	36	Relieved pressure to 30 psig.
1700	292	45	Heater off, opened relief.
1715	210	0	Pump off, loosened lid bolts.
1720	---	--	Run completed.

TABLE 6

Cook 1 - July 19, 1950.

Chips:

wet wt. - 9 lbs.
 % H₂O - 7.0
 OD wt. - 8.37 lbs.

Liquor:

Vol. fresh - 6 gal.
 Vol. used - none
 Liquor/chips - 7.06

<u>Time</u>	<u>T(°F.)</u>	<u>P(psig)</u>	<u>Remarks</u>
0900	---	--	Filled digester, started pump
0915	---	--	Heater on, bolted down lid
0930	160	0	----
1000	198	3	----
1030	226	10	Opened relief to let out air
1100	250	15	Pump knocking
1130	274	29	----
1200	293	42	----
1230	308	58	Reduced pressure to 50 psig
1300	298	44	----
1330	292	38	----
1400	306	50	Bottom flange leaks, bolts tightened
1430	302	46	----
1500	306	50	----
1530	300	44	----
1600	301	44	----
1630	302	46	----

TABLE 6 (Continued)

<u>Time</u>	<u>T(°F.)</u>	<u>P(psig)</u>	<u>Remarks</u>
1700	300	53	----
1730	304	52	----
1800	302	49	----
1830	304	54	----
1900	303	46	----
1930	300	42	----
2000	305	48	----
2030	302	46	Heater off, relief opened
2100	262	20	----
2120	220	0	Cook completed.

Volume liquor recovered	3.5 gal.
Volume fresh wash liquor	2.0 gal. (40%)
Weight wet chips	29 lbs.
% moisture in chips	72%
OD wt. chips	8.1 lbs.
Sp. gr. liquor before cook	1.165 at 60°F.
Sp. gr. liquor after cook	1.190 at 60°F.
pH liquor before cook	8.8 at 25°C.
pH liquor after cook	4.1 at 25°C.
Permanganate number	38.3

TABLE 7

Cook 2 - July 26, 1950.

Chips:

Wet wt. - 9 lbs.
 % H₂O - 7.0
 OD wt. - 8.37 lbs.

Liquor:

Vol. fresh - 6 gal.
 Vol. used - none
 Liquor/chips - 7.06

<u>Time</u>	<u>T(°F.)</u>	<u>P(psig)</u>	<u>Remarks</u>
1000	172	0	Heater, pump on. Bolted lid
1030	198	3	----
1100	228	12	----
1130	257	24	----
1200	284	40	----
1230	302	50	Opened relief briefly
1300	304	50	----
1330	302	48	----
1400	306	50	----
1430	302	48	----
1500	307	50	----
1530	305	50	----
1600	301	48	----
1630	302	52	----
1700	302	50	----
1730	301	49	Heater off, started relief
1800	220	0	Cook completed.

TABLE 7 (Continued)

Volume liquor recovered	3 1/8 gal.
Volume fresh wash liquor	3 gal. (40%)
Weight wet chips	31.5 lbs.
% moisture in chips	74%
OD wt. chips	8.2 lbs.
Sp. gr. liquor before cook	1.165 at 60°F.
Sp. gr. liquor after cook	1.195 at 60°F.
pH liquor before cook	8.65 at 25°C.
pH liquor after cook	4.18 at 25°C.
Permanganate number	38.0

TABLE 8

Cook 3 - August 21, 1950.

Chips:

Wet wt. - 8 lbs.
 % H₂O - 7.8
 OD wt. - 7.38

Liquor:

Vol. fresh - 5.5 gal.
 Vol. used - none
 Liquor/chips - 7.32

<u>Time</u>	<u>T(°F.)</u>	<u>P(psig)</u>	<u>Remarks</u>
1000	178	0	Heater, pump on. Bolted lid
1030	194	3	----
1100	236	16	----
1130	266	31	----
1200	290	47	----
1230	307	54	----
1300	302	60	----
1330	300	51	----
1400	292	47	----
1430	302	52	----
1500	292	48	----
1530	297	52	----
1600	300	50	----
1630	302	58	----
1700	294	44	----
1730	296	46	Heater off. Opened relief
1800	220	0	Cook completed.

TABLE 8 (Continued)

Volume liquor recovered	3 gal.
Volume fresh wash liquor	4 gal. (20%)
Weight wet chips	24.3 lbs.
% moisture in chips	72%
OD wt. chips	6.8 lbs.
Sp. gr. liquor before cook	1.165 at 60°F.
Sp. gr. liquor after cook	1.190 at 60°F.
pH liquor before cook	8.2 at 25°C.
pH liquor after cook	4.6 at 25°C.
Permanganate number	26.5

TABLE 9

Cook 4 - September 19, 1950.

Chips:

Wet wt. - 9 lbs.
 % H₂O - 7.0
 OD wt. - 8.37 lbs.

Liquor:

Vol. fresh - none
 Vol. used - 6 gal.
 Liquor/chips - 7.15

<u>Time</u>	<u>T(°F.)</u>	<u>P(psig)</u>	<u>Remarks</u>
0900	174	0	Heater, pump on. Bolted lid
0930	196	2	----
1000	232	13	----
1030	262	28	----
1100	286	43	----
1130	298	50	----
1200	304	54	----
1230	296	51	----
1300	290	49	----
1330	290	50	----
1400	302	56	----
1430	294	53	----
1500	296	52	----
1530	301	53	----
1600	296	48	----
1630	296	46	Heater off. Opened relief
1700	220	0	Cook completed.

TABLE 9 (Continued)

Volume liquor recovered	3.25 gal.
Volume wash liquor	4 gal (used)
Weight wet chips	30 lbs.
% moisture in chips	74%
OD wt. chips	7.8 lbs.
Sp. gr. liquor before cook	1.182 at 60°F.
Sp. gr. liquor after cook	1.212 at 60°F.
pH liquor before cook	5.2 at 25°C.
pH liquor after cook	4.5 at 25°C.
Permanganate number	26.0

TABLE 10

Cook 5 - December 15, 1950.

Chips:

Wet wt. - 8 lbs.
 % H₂O - 6.0
 OD wt. - 7.52 lbs.

Liquor:

Vol. fresh - none
 Vol. used - 7 gal.
 Liquor/chips - 9.16

<u>Time</u>	<u>T(°F.)</u>	<u>P(psig)</u>	<u>Remarks</u>
1400	170	0	Heater, pump on. Bolted lid
1430	207	2	Let out air
1500	236	12	----
1530	260	23	----
1600	284	38	----
1630	303	54	----
1700	324	83	----
1730	326	90	----
1800	327	92	----
1830	320	88	Burned out heater connection
1900	324	92	Repaired
1930	321	84	----
2000	326	88	----
2030	327	74	----
2100	324	71	Opened relief
2130	260	23	----
2200	218	0	Cook completed.

TABLE 10 (Continued)

Volume liquor recovered	4 1/3 gal.
Volume wash liquor	none
Weight wet chips	28 lbs.
% moisture in chips	76.5%
OD wt. chips	6.58 lbs.
Sp. gr. liquor before cook	1.182 at 60°F.
Sp. gr. liquor after cook	1.206 at 60°F.
pH liquor before cook	5.2 at 25°C.
pH liquor after cook	---
Permanganate number	26.1