4-1968

# The Pulping of Wood with A n-Butyl Alcohol-Water System

John D. Sinkey
*Western Michigan University*

## Recommended Citation

Sinkey, John D., "The Pulping of Wood with A n-Butyl Alcohol-Water System" (1968). *Paper Engineering Senior Theses*. 502.
https://scholarworks.wmich.edu/engineer-senior-theses/502

# THE PULPING OF WOOD WITH A n-BUTYL ALCOHOL-WATER SYSTEM

by John D. Sinkey

A thesis submitted to the
Faculty of the Department of
Paper Technology

in partial fulfillment of the
Degree of Bachelor of Science

Western Michigan University

Kalamazoo, Michigan

April, 1968

# ABSTRACT

Aspen chips were cooked in liquor composed of equal volumes of n-butyl alcohol and water, at reflux and at 150 and 185 degrees Centigrade, in order to investigate the potential use of this organic liquid as a pulping agent. Of particular interest were the effects of adding certain substances to the liquor, the effects of time and temperature, and the effects of liquor pH, as controlled by various reagents. Pulping action increased and yields decreased with increasing digestion time and temperature. No apparent advantage in pulping was demonstrated when polysulfide, dimethyl sulfoxide, or sodium xylenesulfonate was added to the liquors. The optimum pH range for catalysis of the butanol-lignin reaction appeared to be above 3 to 6.5. At severe enough conditions, the formation of wood acids catalyzed the reaction. Greater pulping effects were realized by the addition of mineral acid or $Al_2(SO4)_3$. It appeared advantageous to exercise greater control of pH by using urea or a buffer. $AlCl_3$ was unfavorable as a catalyst, since it seemed to promote hydrolysis of carbohydrates and precipitation of lignin.

## TABLE OF CONTENTS

PAGE

## A.. INTRODUCTION

Aliphatic monohydroxy alcohols have been used for many years in the isolation of lignin, particularly when it was desired to study the properties of this substance. Kleinert and Tayenthal (1) obtained pulped residues from wood cooked with aqueous ethanol solutions above 150° C., with acid catalyst. McMillen and co-workers (2) made a study of both softwoods and hardwoods cooked with n-butanol, with a hydrochloric acid catalyst. Aronovsky and Gortner (3) also investigated the action of several alcohols, including methyl, ethyl, n-propyl, isopropyl, n-, iso-, and tert-butyl, and n-, iso-, and tert-amyl, on aspen sawdust. Of these, n-butyl and n-amyl were found to have the optimum pulping properties.

The experiments described herein were designed to further investigate the action of an aqueous n-butanol system on aspen wood in the presence of an acid catalyst. In particular, it was desired to determine how pulp yields and pulp quality were affected by cooking time and temperature, by the addition of special liquor additives, and by liquor pH as controlled by various reagents.

## B. HISTORICAL BACKGROUND

### 1. Action of Aliphatic Monohydroxy Alcohols

Much work done in the 1930's demonstrated the feasibility of utilizing aliphatic alcohols to dissolve lignin from wood (1-7).

Kleinert and Tayenthal (1) compared lignins obtained from hardwood cooked in non-aqueous ethanol with those obtained from aqueous ethanol liquors. It was found that the former lignins had added alkoxyl groups, but the presence of water during cooking reportedly resulted in lignins containing no other alkoxyl groups than those present in the original wood.

Aronovsky and Gortner (3) found that pulping efficiencies of monohydroxy alcohols were related to water solubilities of the organic reagents. A cook of aspen chips in n-butyl alcohol yielded a pulp with strength properties similar to commercial hardwood alkaline pulp. The spent liquors of aqueous butanol cooks separated into two layers upon cooling. The top alcoholic layer contained organics extracted from the wood, and the bottom water layer contained only small amounts of water-soluble substances. When urea was added to the liquors, yields were generally higher, and pentosans appeared to have been protected.

Aronovsky and Gortner (6) also investigated the pulping action of 6% nitric acid by volume in alcohols, on aspen and jack pine. Experiments were conducted under reflux for two to seven hours, and pulped residues were obtained from both wood species.

In a continuing study of the feasibility of using methanolysis of wood as a commercial process for obtaining pulp and chemical products, Cerny (7) found that the reaction between methanol and wood involves the conversion of carbonyl groups to acetals and ketals, and the formation of methyl ethers from phenolic hydroxyl groups.

## 2. Action of Special Liquor Additives

Since the 1930's, many substances have been found which may exhibit advantageous effects in the pulping of wood, either when used alone or in conjunction with other pulping agents. The possibility of realizing benefits from using some of these substances in the butanol system was considered.

The action of dimethyl sulfoxide (DMSO) on wood has been investigated by several workers (8-11). This reagent yields a well-pulped wood residue under relatively mild conditions. It is catalyzed with mineral acid, and must be in concentration over 50% by volume (in water) to be effective (8,9). It is known, however, that DMSO promotes the solubilizing of pentosans (10). It can be used in conjunction with $SO_2$ or $Cl_2$ to produce alpha cellulose from wood (11). DMSO has also been shown to increase pulping effects in kraft liquor and in the hydrotropic pulping process (12).

The hydrotropic process (13) is based on the fact that lignins are soluble in saturated or near-saturated solutions of the so-called hydrotropic salts. Sodium xylenesulfonate is a classic example of such a salt. As mentioned above, the use of a hydrotropic salt in conjunction with DMSO has been shown to increase benefits above what is achieved with either agent alone.(12).

Polysulfide pulping (14-16) has been on the scene for many years, and has been receiving increasing attention recently in the kraft process. Its chief attraction is the ability of polysulfide to protect pentosans (16).

## 3. Development of the Problem

The present study was, for the most part, an extension of Aronovsky's work with the n-butyl alcohol-water system and aspen wood (3). Most of his experiments were carried out at 180°-190° C., in the time range of three to four hours. Thus it was desired to investigate other temperatures (110° and 150° C.), and other times (one and two hours). The alcohol concentration which he used most, 1:1 alcohol to water ratio by volume, was also used in these experiments. Since Aronovsky obtained pulped residues in a butanol-nitric acid system under reflux (6), several reflux cooks were planned as preliminary "screening" experiments.

In all the references on alcohol pulping which were investigated, mineral acid was used as a catalyst. It appeared that the pH of the system had to be acidic to allow the butanol-lignin reaction to proceed. When Aronovsky (3) added urea to the butanol-water liquor, thus neutralizing wood acids as they were formed during digestion, he obtained higher pulp yields. In addition, the wood residues had higher lignin, Cross and Bevan cellulose, alpha cellulose, and much higher pentosans contents. He then postulated that optimum pulp might be obtained if enough urea were added to maintain a slightly acid pH throughout the cook. Thus the effects of the pH of this aqueous alcohol system seemed quite interesting. It was planned in this study to investigate the effects of controlling liquor pH with hydrochloric acid of various concentrations, aluminum chloride, an acetic acid-sodium acetate buffer, urea, and aluminum sulfate.

## EXPERIMENTAL

### 1. Wood and Reagents

The wood used in this study was in the form of aspen chips, supplied by Nekoosa-Edwards, Nekoosa, Wisconsin. The chips used in all cooks were 49 to 50% solids. The size fraction used was 1/2 to 3/4 inch.

All reagents used were C.P. or U.S.P. grade. All water used was distilled.

### 2. Bomb Digester

The apparatus for digester cooks was a thermostatically controlled oil bath unit. A frame containing six stainless steel bombs or autoclaves, each of about one liter capacity, was immersed in the oil bath. The bombs are bolted into the frame, and the frame is immersed with block and tackle into the hot oil. The frame rotates slowly during the cook. A thermograph records oil temperature constantly.

### 3. General Procedure: Reflux Cooks

For the reflux cooks, a laboratory heating mantle and Florence flasks fitted with water-cooled condensers were used.

The wood (25.0 g. oven-dry basis) and liquor were added to the flask, and the condenser was fitted. The system was then brought to the liquor boiling temperature and held there for the desired time period. Liquor volume to wood weight ratio was about five to one. When the cooking time had elapsed, the flask was removed from the mantle, and its contents were quantitatively transferred to a Büchner funnel. The liquor thus removed was stored in bottles. The wood residue was then washed on the Büchner funnel successively with n-butanol, dilute sodium hydroxide, and cold water. It was finally stored in plastic bags for subsequent yield determinations. Yields were run on the entire wood residue sample, by determining percent solids of the material.

### 4. General Procedure: Digester Cooks

The wood (100.0 g. oven-dry basis) and the liquors (8:1 liquor volume to wood weight ratio) were charged into the autoclaves. The latter were put into the frame, immersed into the preheated oil, and started to rotate. At the end of the cooking period, the frame was removed from the oil, and the bombs were taken from the frame and sprayed with cold water from a hose. The contents of each bomb were individually transferred to a Büchner funnel, and the wood residue washed several times with water. It was then subjected to 400 revolutions in the Tappi disintegrator. The resultant "pulp" was dewatered on the Büchner funnel, and stored in Mason jars for subsequent yield determination on an aliquot.

## D. DISCUSSION

The results of the present work are presented in Tables I, II, and III. No duplicate determinations were made.

### 1. Reflux Cooks (Table I)

#### a. The butanol-DMSO system

Comparison of cooks R1 through R4 shows that increasing the amount of DMSO in non-aqueous butanol increases the pulping effects, as evidenced by the appearance of the wood residues, and by the decreased yields.

b. The effect of time

Cooks R5, R6, and R7 demonstrate that increasing digestion time for the aqueous butanol system results in increased pulping and decreased pulp yields.

c. The effect of hydrotropic salt

Since the wood residues of cooks R8 through R11 were not defibered and washed well, the retention of the hydrotropic salt in the chips during yield determinations made the yield values meaningless. But observation of the chips after treatment demonstrates that no apparent advantage is obtained, under reflux at least, by adding sodium xylenesulfonate to the butanol system. Evidence presented here is inconclusive as to potential advantages of adding hydrotropic salt to a butanol system under other cooking conditions.

d. Amount of HCl catalyst

Comparison of R7 and R12 through R14 reveals that the amount of acid catalyst has a direct relationship upon the yield of the butanol "pulp". Indeed, it is quite conceivable that the acid hydrolysis of carbohydrates increases when increasing amounts of HCl are added to the system, thus decreasing yield rapidly. Comparison of cook R1 with R15 would indicate that in this case, most of the yield reduction is due to the alcohol, however.

2. Digester Cooks (Tables II and III)

a. Effect of HCl catalyst

Quite apparently a temperature of 185° C. is sufficient to liberate acetic and formic wood acids, which may catalyze the reaction between wood and butanol. D1A and D2A yields were rather low, approaching those of catalyzed cooks in the respective series. Moreover, the pulps obtained in D1A and D2A were similar to those of catalyzed cooks.

As increasing amounts of HCl catalyst were added to liquors of one-hour cooks (D1B, C, D), yields decreased significantly. This effect was especially noticeable when initial liquor pH was brought from 3 to 1 by the HCl. Similar results were noticed in the two-hour cooks (D2B, C, D), although the yield reductions due to HCl were of lesser magnitude.

b. Effect of buffer

The acetic acid-sodium acetate buffered liquors (D1F and D2F) demonstrate that the maintenance of pH by buffer may be desirable. It will be noted that these two cooks, buffered to pH 5, were of higher yields than cooks brought to an initial pH of 5 (D1B and D2B respectively). In addition, the buffered wood residues retained their fibrous chip form more that the corresponding unbuffered "pulps". Thus it would seem that the unbuffered liquor attacks carbohydrates more than buffer solutions.

c. Effect of $AlCl_3$

The effect of the Lewis acid aluminum chloride is interesting. Although the initial pH of the solution is near 3, the system undoubtedly becomes very acidic under cooking conditions. The reaction involved is:

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl.$$

The HCl liberated by this hydrolysis of $AlCl_3$ quite apparently causes severe attack of carbohydrates, even after one hour at 185° C. (D1E and D2E). Furthermore, the wood residue left after these cooks appeared to be lignin. $AlCl_3$ evidently enhances precipitation of lignin. (It has been noted that lignin can be precipitated from spent sulfite liquor with basic $AlCl_3$ (17).)

Cook series D3 (Table III) was run primarily to further investigate the effects of $AlCl_3$ at lower temperatures, and at lower concentrations. Comparison of control D3A with D3B shows that 0.1% $AlCl_3$ did not attack carbohydrates to any extent (high yield), even though the initial pH was about 3.. In addition, it is conceivable that even this small amount of Lewis acid promoted the precipitation of lignins which would otherwise have been dissolved by the butanol.

Increasing the $AlCl_3$ concentration to 2.0% on O.D. wood (D3C) resulted in a lower yield than the HCl control (D3A). This implies the existence of an effect similar to that observed in D1E and D2E. The $AlCl_3$ pulp appeared less fibrous than the HCl catalyzed pulp, the former appearing more degraded.

In cook D3E, the urea appeared to have neutralized the Lewis acid. Possibly the butanol reaction was not catalyzed. There may have been an excess of the basic urea, and/or the urea may have protected carbohydrates while the $AlCl_3$ present inhibited dissolution of lignin by butanol.

d. Effect of time and temperature

Comparison of cook D1C with D3A shows a slight increase in yield with this 35° decrease in temperature. Doubling cooking time from one hour to two hours at 185° C. (cooks D1 and corresponding cooks of D2) resulted in yield decrease of 5-13%, depending on the system.

e. Effect of polysulfide

It appears that polysulfide in the butanol system (D3F) may protect carbohydrates. However, the high pH necessary for its existence in solution (about 9.5) probably hinders the butanol-lignin reaction.

f. Effect of $Al_2(SO_4)_3$

Cook D4A demonstrates that aluminum sulfate could serve as a suitable catalyst for the butanol-lignin reaction. This reagent is not as potent in this role as are HCl and $AlCl_3$.

g. Effect of DMSO

Quite an interesting and as yet unexplained phenomenon occurred in cook D4C. The DMSO apparently inhibited the effects of the butanol. Yield was high, and chips appeared unchanged, except for a darkening, Such was unexpected in view of reflux cooks R1-R4, and the literature. Evidently DMSO increases pulping effects of non-aqueous butyl alcohol, but has opposite effects on the aqueous alcohol system.

### h. Effect of urea

Cook D4D (compared with control D3A) demonstrates that urea may protect carbohydrates from dissolution by control of pH. It is evident, however, that even 1.0% urea is too much at these conditions. It probably kept the pH alkaline here. At higher temperature, this amount of urea would likely be quite beneficial, with action similar to that of a buffer solution.

## E. CONCLUSIONS

Pulp yields decrease with increasing cooking time and temperature in the butanol-water system.

No apparent advantage was demonstrated by adding the hydrotropic salt sodium xylenesulfonate to either the aqueous or the non-aqueous butanol system at reflux conditions. Evidence was inconclusive as to the effect of this reagent at other cooking conditions.

Increasing the amount of dimethyl sulfoxide in the non-aqueous butanol system increases the pulping effects of the butyl alcohol. The addition of 20% by volume of DMSO to aqueous butanol apparently hinders the pulping action.

No apparent benefit is realized by adding polysulfide to the butanol-water system, undoubtedly because of the high pH required for the former to exist in the system.

Under reflux conditions, increasing the amount of HCl catalyst decreases yield significantly, probably because of increased hydrolysis of carbohydrates. At 185° C., wood acids alone evidently provide sufficient acidity to catalyze the butanol-lignin reaction. Adding increasing amounts of HCl catalyst to the aqueous butanol system under these conditions gives more and more reduced yields.

It is conceivable that optimum pulp could be obtained by controlling pH during digestion, either with urea or a buffer. The optimum pH range appears to be above 3 up to about 6.5.

No unfavorable effects are noted when $Al_2(SO_4)_3$ is used as a catalyst in the butanol-water system. If $AlCl_3$ is used as a catalyst, however, the hydrolysis of this Lewis acid during digestion apparently promotes attack of carbohydrates. In addition, $AlCl_3$ evidently inhibits dissolution of lignins.

The n-butanol-water system shows potential advantages as a pulping process, and possibly as a process for obtaining chemical products from wood.

The odor is less of a problem than with kraft, for example. The spent liquors could conceivably be recovered economically, either by distillation, or by ion exchange, electrodialysis, or chemical precipitation. The lignins which can be isolated from these spent liquors are not contaminated with inorganics (such as sulfur), and are thought to be in a form similar to protolignin. These lignins would also be expected to have lower toxicity than lignins from other pulping liquors (potential use as fertilizers). And finally, the pulps obtained are brown to gray, with strength properties similar to hardwood alkaline pulps.(3).

## F. RECOMMENDATIONS

Since only a limited amount of time was available in this study to carry out digester cooks, it would be desirable to make duplicate cooks, and run analyses on the wood residues obtained. Lignin, pentosans, and alpha cellulose determinations would be of value in validating the evidence presented herein.

In addition, study of the effects of other variables is recommended. Investigation of the effect of hydrotropic salts under more severe digestion conditions may prove profitable. Since the lignins produced in this process are relatively uncontaminated, a study of these by-products may also prove interesting.

Aronovsky (3) has noted the possibility of the butyl alcohol becoming saturated before the end of the cook. He has found some benefit in pumping in fresh hot alcohol to replace spent liquor. This was done at several time intervals during digestion. Hence further work regarding the solubility of wood materials in butyl alcohol may be enlightening.

Finally, if it were desired to scale up the process, the various aspects of liquor recovery should be investigated. Since 100 parts of water dissolve 8 to 9 parts of n-butyl alcohol, the aqueous portion, as well as the alcoholic layer, would have to be used conservatively in order to realize economic advantage.

TABLE I: SUMMARY OF REFLUX COOKS*

| CODE | LIQUOR | ADDITIVES | cc. CONC. HCl ADDED | TEMP. (°C.) | TIME (Hr.) | YIELD (%) | COMMENTS ON PULP |
|---|---|---|---|---|---|---|---|
| R1 | 100% B | - | 10.0 | 118 | 3.0 | 69.6 | soft, pliable |
| R2 | 67%B, 33%D | - | 10.0 | 106 | 3.0 | 63.6 | some disintegrated chips |
| R3 | 33%B, 67%D | - | 10.0 | 100 | 3.0 | 62.9 | mostly fibrous |
| R4 | 100% D | - | 10.0 | 94 | 3.0 | 61.7 | all fibrous |
| R5 | 50%B, 50%W | - | 10.0 | 109 | 1.0 | 89.7 | soft |
| R6 | 50%B, 50%W | - | 10.0 | 109 | 2.0 | 82.0 | quite pliable |
| R7 | 50%B, 50%W | - | 10.0 | 109 | 3.0 | 78.5 | quite pliable |
| R8 | 100% W | 60g.H | 0.1 | 102 | 3.0 | 146.8** | hard chips |
| R9 | 50%B, 50%W | 60g.H | 0.1 | 112 | 3.0 | 140.2** | hard chips |
| R10 | 100% B | 60g.H | 0.1 | 122 | 3.0 | 157.2** | hard chips |
| R11 | 50%B, 50%W | 5g.H | 0.1 | 110 | 3.0 | 111.4** | hard chips |
| R12 | 50%B, 50%W | - | 0.1 | 110 | 3.0 | 96.5 | hard chips |
| R13 | 50%B, 50%W | - | 1.0 | 110 | 3.0 | 94.9 | softened |
| R14 | 50%B, 50%W | - | 5.0 | 110 | 3.0 | 90.4 | quite soft |
| R15 | 100% W | - | 10.0 | 101 | 3.0 | 92.0 | brittle chips |

B: n-butyl alcohol
W: distilled water
D: dimethyl sulfoxide
H: sodium xylenesulfonate

* 25.0 g. O.D. wood, 5:1 liquor volume to wood weight ratio

** Wood residues of R8, 9, 10, 11 not washed sufficiently to rid them of excess salt

TABLE II: SUMMARY OF DIGESTER COOKS

| CODE | TEMP.(°C.) | TIME (Hr.) | SYSTEM* | INITIAL pH | % YIELD | COMMENTS ON PULP |
|---|---|---|---|---|---|---|
| D1A | 185 | 1.0 | no catalyst | 6.5-7 | 72.1 | semi-pulped |
| D1B | 185 | 1.0 | HCl | 5 | 69.5 | semi-pulped |
| D1C | 185 | 1.0 | HCl | 3 | 68.5 | semi-pulped |
| D1D | 185 | 1.0 | HCl | 1 | 57.9 | semi-pulped |
| D1E | 185 | 1.0 | 5.0g. $AlCl_3$ | 3 | 7.6 | non-fibrous black "mud" |
| D1F | 185 | 1.0 | 1.0g. HAc,<br>1.8g. NaAc | 5 | 70.5 | slightly pulped |
| D2A | 185 | 2.0 | no catalyst | 6.5-7 | 64.3 | semi-pulped |
| D2B | 185 | 2.0 | HCl | 5 | 57.4 | semi-pulped |
| D2C | 185 | 2.0 | HCl | 3 | 55.0 | semi-pulped |
| D2D | 185 | 2.0 | HCl | 1 | 53.4 | semi-pulped |
| D2E | 185 | 2.0 | 5.0g. $AlCl_3$ | 3 | ---- | non-fibrous black "mud" |
| D2F | 185 | 2.0 | 1.0g. HAc,<br>1.8g. NaAc | 5 | 59.0 | slightly pulped |

* See "Note", Table III

N.B.: All wood residues, unless otherwise noted, were light brown in color.

TABLE III: SUMMARY OF DIGESTER COOKS (CONT.)

| CODE | TEMP.( C.) | TIME (Hr.) | SYSTEM* | INITIAL pH | % YIELD | COMMENTS ON PULP |
|---|---|---|---|---|---|---|
| D3A | 150 | 1.0 | HCl | 3 | 72.9 | semi-pulped |
| D3B | 150 | 1.0 | 0.1g. $AlCl_3$ | 3.5 | 93.8 | hard chips, slightly darkened |
| D3C | 150 | 1.0 | 2.0g. $AlCl_3$ | 3 | 61.9 | pulped, dark brown |
| D3E | 150 | 1.0 | 2.0g. $AlCl_3$, 3.0g. urea | - | 94.0 | hard chips, much darkened |
| D3F | 150 | 1.0 | 6% polysulfide | 9.5 | 91.6 | slightly softened, darkened |
| D4A | 150 | 1.0 | 5g. $Al_2(SO_4)_3$ | 3 | 67.5 | pulped |
| D4C | 150 | 1.0 | 20% vol. DMSO, HCl | 5 | 92.3 | hard chips, darkened |
| D4D | 150 | 1.0 | 1.0g. urea, HCl | 5 | 94.7 | hard chips, slightly darkened |

* Note: The system includes the noted substances added to 100.0 g. O.D. basis wood in a 50-50% by volume liquor of water and n-butyl alcohol; liquor volume to wood weight ratio was 8:1.

N.B.: All wood residues, unless otherwise noted, were light brown in color.

## LITERATURE CITED

1. Kleinert, T., and Tayenthal, K., U.S. pat. 1,865,567 (1932)

2. McMillen, J.M., Gortner, R.A., Schmitz, H., and Bailey, J., Ind. Eng. Chem. 30, No. 12: 1407-1409 (Dec.,1938)

3. Aronovsky, S.I., and Gortner, R.A., Ind. Eng. Chem. 28, No. 11: 1270-1276 (Nov., 1936)

4. Aronovsky, S.I., U.S. pat. 2,037,001 (April 14, 1936)

5. Bailey, A.J., Pacific Pulp Paper Ind. 14, No. 3: 24-27 (March, 1940)

6. Aronovsky, S.I., and Gortner, R.A., Ind. Eng. Chem. 29, 1431 (1937)

7. Cerny, M., Chem. Zvesti. 20 (2): 132 (1966)

8. ----, Pulp Paper Mag. Can. 8, 127 (1958)

9. Hossain, Shafi, U.S. pat. 2,901,389 (1960)

10. ----, Drevarsky Vyskum., No. 4: 187-201 (1964)

11. Anon., Can. Chem. Proc. 46, No. 12: 34-35 (Dec., 1962)

12. Borisek, R., Bull. Inst. Politeh. Iasi N.S. 11 (15): special no.: 85 (1965)

13. McKee, R.H., Paper Ind. 42, No. 4: 255-257 (July, 1960)

14. Drewson, E., U.S. pat. 996,225 (1911)

15. Spence, G.[illegible]., Paper Trade Journal 71 (11): 24 (1920)

16. Ekman, K., and Järvelä, Oiva, Tappi 50, No. 2: 75-77 (Feb.,1967)

17. Morimoto, T., U.S. pat. 3,270,002(Aug. 30, 1966)