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Effect of Pulping Time on the Chemical Composition of Cold Soda Pulp

Timothy K. Estes
Western Michigan University

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EFFECT OF PULPING TIME ON THE CHEMICAL
COMPOSITION OF COLD SODA PULP

A
dissertation
submitted to the faculty
of
Western Michigan University

by
Timothy K. Estes

In partial fulfillment of
the prerequisites for the degree
of
Bachelor of Science

June, 1962
ACKNOWLEDGEMENT

I would like to express my appreciation to Dr. Robert A. Diehm of the Department of Paper Technology, Western Michigan University, without whose help this thesis would not have been possible.
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LITERATURE SURVEY

Introduction

The cold soda pulping process was developed by the Forest Products Laboratory, Madison, Wisconsin, around 1950. It is a high yield process in which wood chips are softened by reacting with sodium hydroxide and then defibberized by mechanical refining. The yield is usually between 80% - 95%.

Cold soda pulps with the following characteristics were used for this literature survey: The yields were between 80%-95%. The pulping temperatures were less than 40° C. The pulping operations were conducted under atmospheric pressure.

Research Reported

The first technical article on cold soda pulping was written by Brown and McGovern in 1950 (1). In their work they treated quaking aspen wood chips with sodium hydroxide. They used two concentrations of sodium hydroxide, 24 g/l. and 63 g/l. Their pulping reaction times were ¼, ½, 1, 1½, 2, and 5 hours. Their temperatures were 25°, 60°, and 90° C. The liquor to wood ratio was five to one. Besides the strength properties of the pulps they also tested lignin, alpha cellulose, and holocellulose. Table I shows part of
TABLE I

Results of Mild Treatments of Aspen Chips with Sodium Hydroxide by Brown and McGovern

<table>
<thead>
<tr>
<th>Time</th>
<th>Yield</th>
<th>% Lignin</th>
<th>% Hemicellulose</th>
<th>% Alpha-cel lulose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Original Wood</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>95.3%</td>
<td>17.7%</td>
<td>78.6%</td>
<td>48.6%</td>
</tr>
<tr>
<td></td>
<td>24.1 grams NaOH per liter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¼</td>
<td>94.6%</td>
<td>16.8%</td>
<td>79.4%</td>
<td>48.7%</td>
</tr>
<tr>
<td>½</td>
<td>92.8%</td>
<td>16.6%</td>
<td>78.6%</td>
<td>49.7%</td>
</tr>
<tr>
<td>1</td>
<td>92.1%</td>
<td>16.8%</td>
<td>76.6%</td>
<td>48.7%</td>
</tr>
<tr>
<td>1½</td>
<td>91.3%</td>
<td>17.3%</td>
<td>71.2%</td>
<td>47.4%</td>
</tr>
<tr>
<td>2</td>
<td>90.4%</td>
<td>16.8%</td>
<td>68.9%</td>
<td>46.7%</td>
</tr>
<tr>
<td></td>
<td>63.0 grams NaOH per liter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¼</td>
<td>91.8%</td>
<td>17.4%</td>
<td>77.2%</td>
<td>48.7%</td>
</tr>
<tr>
<td>½</td>
<td>90.3%</td>
<td>18.7%</td>
<td>72.0%</td>
<td>48.2%</td>
</tr>
<tr>
<td>1</td>
<td>88.8%</td>
<td>16.9%</td>
<td>70.0%</td>
<td>48.8%</td>
</tr>
<tr>
<td>2</td>
<td>88.4%</td>
<td>16.4%</td>
<td>69.5%</td>
<td>49.1%</td>
</tr>
</tbody>
</table>
their results. Figure 1 shows the effect of lignin with time. The solid line is the line drawn by Brown and McGovern after considering all the data including the temperatures other than $25^\circ C$. Figure 2 is the same as Figure 1 except it shows the effect of alpha cellulose with pulping reaction time. Figure 3 shows the effect of holocellulose upon pulping reaction time and Figure 4 shows the pulp yield with the different pulping times. In all cases the solid lines were the lines drawn by Brown and McGovern and the broken lines were not. This work was the only work extensively reported in which the pulping reaction time was changed and the chemical composition of the pulp was determined.

Brown and McGovern also did some further work (2) in which different woods (white oak, jack pine, western hemlock, sweet gum, cottonwood, red alder, red oak and aspen) were tested in the cold soda pulping operation. However for most of this work only the concentration of the sodium hydroxide was changed and only the strength of the pulps was determined. Table II shows part of their information on aspen pulp.

Brown (3) also reported on studies of southern oak, sweetgum, and cottonwood. Yield and strength were determined for different times, temperatures, and pressures.

The only other information on the cold soda pulping
Figure 1
Percent Lignin vs. Pulping Time
by Brown and McGovern

Figure 2
Percent Alpha Cellulose vs. Pulping Time
by Brown and McGovern
Figure 3
Percent Holocellulose vs. Pulping Time
by Brown and McGovern

Figure 4
Percent Yield vs. Pulping Time
by Brown and McGovern
TABLE II

Effect of Sodium Hydroxide Concentration on Yield by Brown and McGovern

Aspen Wood at 25° C.

<table>
<thead>
<tr>
<th>Conc. NaOH</th>
<th>Time</th>
<th>NaOH consumed</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>24g/l</td>
<td>2 hr.</td>
<td>5.5%</td>
<td>90.4%</td>
</tr>
<tr>
<td>50g/l</td>
<td>2 hr.</td>
<td>6.7%</td>
<td>89.0%</td>
</tr>
<tr>
<td>63g/l</td>
<td>2 hr.</td>
<td>7.2%</td>
<td>88.4%</td>
</tr>
</tbody>
</table>
of aspen wood was from a report by Foster (4). He treated aspen chips for two hours at 25°C with a sodium hydroxide solution of 53g/l. He then tested the pulp for lignin, alpha cellulose, and holocellulose. Table III shows his results.

Ceragioli (5) prepared an extensive report using poplar wood. With a five hour reaction time at 20°C he used sodium hydroxide concentrations of 10, 25, 40, 55, and 70 g/l. He also tried two different solid to liquid ratios of one to seven and one to ten. In one experiment he also varied the time from one half hour to two hours. However this experiment was run at 90°C. His tests included the amount of lignin and hemicelluloses, along with the strength properties.

Poplar wood was also the study of Colombo, Corbellta, Gaetani, Pirotta, and Sartori (6). They cooked from two to five hours in an open vessel with 20 to 100 grams of sodium hydroxide per liter at 25°C to 80°C.

The influence of temperature was studied by Runkel and Schambach (7). They used temperatures of 0°C, 20°C, 40°C, 60°C, 70°C, 100°C, and 150°C on beech wood. Paper chromatography was used to analyze the different hemicelluloses. Lignin and yield were also determined. Table IV shows part of these results.

Bhat and Virmani (8) treated blue gum at temperatures of 30°C, 50°C, and 70°C. Sodium hydroxide concentrations of 2%, 3%, 4%, and 5% were used bases on the oven dry weight of the pulp. Only strength was
TABLE III

Chemical Composition of Aspen Pulp and Wood by Foster

<table>
<thead>
<tr>
<th>Weight Fraction</th>
<th>Wood</th>
<th>2 Hr. Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives (Alcohol-Benzene)</td>
<td>3.4%</td>
<td>0.5%</td>
</tr>
<tr>
<td>Lignin</td>
<td>21.1%</td>
<td>17.4%</td>
</tr>
<tr>
<td>Holocellulose</td>
<td>90.3%</td>
<td>71.7%</td>
</tr>
<tr>
<td>Alpha Cellulose</td>
<td>50.3%</td>
<td>49.3%</td>
</tr>
<tr>
<td>Hemicellulose (by difference)</td>
<td>40.0%</td>
<td>22.4%</td>
</tr>
</tbody>
</table>

TABLE IV

Effect of Temperature upon Lignin and Yield of Beech Wood by Runkel and Schambach

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Lignin</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0° C.</td>
<td>21.2%</td>
<td>94.4%</td>
</tr>
<tr>
<td>20° C.</td>
<td>19.7%</td>
<td>92.2%</td>
</tr>
<tr>
<td>40° C.</td>
<td>19.1%</td>
<td>90.2%</td>
</tr>
<tr>
<td>70° C.</td>
<td>17.7%</td>
<td>86.1%</td>
</tr>
<tr>
<td>100° C.</td>
<td>18.2%</td>
<td>85.5%</td>
</tr>
<tr>
<td>150° C.</td>
<td>15.8%</td>
<td>79.4%</td>
</tr>
<tr>
<td>Orig. Wood</td>
<td>22.5%</td>
<td>100.0%</td>
</tr>
</tbody>
</table>

2.4% NaOH
Alkali consumption was of interest to Watson, Dadswell, and Stewart (9) in their study of pulps from eucalyptus regnans. They carried out experiments using different temperatures, times, alkali concentrations, chip sizes, and amounts of moisture in the chips at the start.

Conclusions From Research Reported

Cold soda pulping does not remove much lignin. Brown and McGovern (1,2) in their work show that little or no lignin is removed (Table I, Figure 1). Colombo and his co-workers (6) claimed that there was almost no lignin lost in their work on poplar wood. While Ceragioli and his co-workers (5) showed a removal of 5%-8% of the lignin in poplar wood. Runkel and Schambach (7) showed losses ranging from 1%-7% depending upon the temperature. They point out that delignification is incomplete even at the highest temperatures (150°C). They also state that a type of artificial lignin is made at higher temperatures (Table IV). Casey (10) also states that cold soda pulping is not specific for lignin removal in pulping at atmospheric pressure for one to two hours. In all cases it is safe to say that in a cold soda pulping operation well over half of the original lignin
remains in the final cold soda pulp.

Brown and McGovern showed that cold soda pulping does not remove alpha cellulose (Figure 2). Colombo and co-workers (6) also found this true.

It is generally agreed that cold soda pulping reduces the amount of hemicelluloses (1, 2, 4, 5, 6, 7). Brown and McGovern (1, 2) state in their articles that the loss of yield is due to a loss of hemicelluloses (Table I, Figures 1-3). Colombo and co-workers (6) agree with this pointing out that only the accessible hemicelluloses are removed from the wood.

The cold soda pulping process is especially applicable to hardwoods because the mechanical refining reduces the strength of softwoods until they are not any stronger than hardwoods (2). Aspen wood has often been used in cold soda pulping. Quaking aspen has about 82% holocellulose. It has more holocellulose than other common hardwoods and softwoods (10). Aspen is one of the strongest cold soda pulps (2).

The strength increases as the yield decreases (2, 3, 5). The strength also improves with caustic consumption (8). The strength is increased by increasing the time temperature or pressure (3). Thus a more drastic treatment increases strength and decreases yield (5).

In their first report Brown and McGovern (1) found the optimum conditions (those with the best
yield and strength) with a two hour cook at 25°C and a sodium hydroxide concentration of 24 grams per liter. This gives a yield of 91%. In a later report (2) a yield of 88%-90% is considered optimum with regard to pulp strength.

Theory of Cold Soda Pulping

Cold soda pulping is mainly a removal of hemicelluloses rather than lignin or alpha cellulose (1). There is much disagreement over the definition of hemicellulose. Most people admit that the hemicelluloses are soluble in a cold five percent aqueous sodium hydroxide solution, although it may take a long time (10,11). For this report hemicellulose will be defined as that portion of wood soluble in 17.5% sodium hydroxide under certain specified conditions and alpha cellulose will be that portion of the holocellulose insoluble in 17.5% sodium hydroxide under certain specified conditions (10,12). Thus it would seem by the definition of hemicellulose that some of the hemicelluloses would be removed and none of the alpha cellulose would be removed in the cold soda pulping.

One theory on what happens in cold soda pulping was presented by Watson and co-workers (9). They suggest that during alkaline treatment chemical bonds associated with fiber adhesion are weakened. This weakening, rather than the small amount of lignin removed
enables the chips to be defibered mechanically without undue damage.

Runkel and Schambach (7) conducted much research in the noncellulose constituents of wood which are removed in the caustic pulping process. It is these noncellulose (non-lignin) constituents which they believe will explain the relatively good defibration of the softened chips in combination with a very high yield.

Hemicellulose (12) may be broken down into beta and gamma cellulose. Beta cellulose is that portion of the cellulose which is soluble in 17.5% sodium hydroxide but insoluble when the hydroxide is neutralized. Gamma cellulose is soluble in both 17.5% sodium hydroxide and when the solution is neutralized. Some people (10) feel that beta cellulose gives a measure of the degraded cellulose while gamma cellulose indicates the natural hemicellulose.

If this is true then in cold soda pulping it would be suspected that the gamma celluloses are removed. By removing the gamma cellulose less alpha cellulose would be degraded to beta cellulose, thus there would be less beta cellulose and possibly more alpha cellulose.
EXPERIMENTAL PROCEDURE

Preparation of Pulps

Chips

The wood used for the pulp was quaking aspen. The wood had been chipped in a commercial chipper and then the chips were refrigerated to prevent them from drying out or spoiling. The chips contained about 35% moisture.

Pulping Liquor

The pulping liquor was made by dissolving sodium hydroxide (white caustic) in water and then standardizing with a standard acid. The liquor was 1.325 N, or 53 grams per liter, or 4.98% by weight sodium hydroxide.

Pulping Reaction Time

Each pulping operation was conducted by filling a wide mouth one gallon jar with a known amount of chips and then adding the pulping liquor (5% caustic). The ratio of liquor to oven dry chips was about seven to one. The jar was immediately sealed and placed on a bottle rotater. The bottle was then rotated at about thirty revolutions per minute for the duration of the pulping reaction time. Immediately before the end of the pulping reaction time a small portion of the pulping liquor was removed and later titrated for the amount
of caustic left in solution.

Refining

At the end of the pulping reaction time the pulp was passed through a Bauer laboratory refiner which had been previously fitted with course breaker plates. The pulp was further broken up by passing it again through the refiner. After this the course plates were removed and fine plates were inserted. The distance between the plates was adjusted so that the motor required three amperes of current when only a moderate amount of water was flowing through the refiner. The broken up pulp was then passed through the fine plates of the refiner five times.

Screening

After refining the pulp was diluted to about 0.5% solids and passed through a Valley flat bed screen which was equipped with a ten cut (0.010 inch) slotted screen. The pulp was then caught in a 50 mesh tub screen where the excess water was removed. The fines which passed through the tub screen flowed directly to the sewer with no attempt to determine the amount which was lost by this screening. The excess water was squeezed out of the accepted pulp and the pulp was then spread out in the air to dry.

Number of Pulps

Three complete runs were made; one having a half
hour reaction time, one having an hour reaction time, and one having a two hour reaction time. In all runs room temperature (about 25°C) and atmospheric pressure were used.

Also a set of unreacted wood chips were air dried and then passed through a hammer mill which broke the chips into a fine sawdust.

Testing

The three pulps plus the original wood were tested for the following; yield, lignin, alcohol benzene extractives, alpha cellulose, beta cellulose, and gamma cellulose.

Yield

Yield was determined as the oven dry weight of the accepted pulp divided by the oven dry weight of the pulp chips. The accepted pulp was that portion of the pulp which passed through the 0.010 inch slot screen but did not pass through the 50 mesh tub screen. The oven dry weight was determined after storing the pulp in about 17% solids condition for two weeks under refrigeration. In addition the oven dry weight of the material which would not pass through the slot screen (large rejects) was also determined.
Lignin

Lignin was tested according to Tappi method T 13 m-54. In this method wood is treated with 72% sulfuric acid, the carbohydrates are hydrolyzed leaving an insoluble residue which is determined as lignin. The wood is extracted first to remove extractives which may be retained in the lignin determination. The wood was extracted with alcohol-benzene solution but it was not extracted with only alcohol. In addition it was not corrected for ash.

Because of the large amount of lignin in all the pulps all determinations were made by the method for determination of lignin in wood. It was found advantageous to determine all four samples at the same time because minor variations in the temperature affected the results slightly and this way they were all affected equally.

Alcohol-Benzene Extractives

Alcohol-benzene extractives were determined by Tappi method T 6 m-59. In this extraction waxes, fats, resins, and certain other ether-insoluble components, including possibly portions of the so called wood gums and other water soluble components are removed. The weight of the extractives was determined both by the loss of weight in the pulp and the gain of weight of the flask which collected the extractives.
Alpha Cellulose

Alpha cellulose was determined according to Tappi method T 203 m-58. The alpha cellulose is the weight of the pulp which is not soluble in 17.5% sodium hydroxide at 20° C. The results were corrected for lignin but were not corrected for ash.

Beta Cellulose

Beta cellulose was also determined according to Tappi method T 203 m-58. Beta cellulose is soluble in 17.5% sodium hydroxide but insoluble when the solution is neutralized with acid. Beta cellulose is determined volumetrically by oxidation with dichromate. It is the difference between the combined beta plus gamma cellulose and the gamma cellulose.

Gamma Cellulose

Gamma cellulose was also determined according to Tappi method T 203 m-58. Gamma cellulose is soluble in 17.5% sodium hydroxide and also when the solution is neutralized with acid. Gamma cellulose is determined volumetrically by oxidation with dichromate. It was found that after the addition of the potassium iodide in the beta and gamma cellulose determinations, there was a slight tendency for the free iodine to escape from the flask giving erratic results. This trouble was overcome by keeping the flask covered during the five minute waiting period.
EXPERIMENTAL RESULTS

Table V shows the results of the testing. In most cases two or more determinations were made. The column marked "error" takes into account these differences. Table VI is the same data only the figures are adjusted slightly so that they add up to 100%.

Chemical Consumption

The amount of caustic consumed is proportional to the length of the reaction time (Figure 5). However this proportionality does not hold between zero and one half hour. Instead the amount of caustic consumed increases very rapidly during this first fifteen minutes and then levels out to a definite proportion. These results agree with the literature. The large initial consumption at the beginning may be due to neutralization or adsorption of the sodium hydroxide by the wood chips. Since the caustic consumed is proportional to the time, then all of the following graphs if plotted against caustic consumed would look the same as when plotted against pulping reaction time.

Yield

The yield or percent accepts was 64.7% for the half hour pulp, 75.2% for the hour pulp and 81.2% for the two hour pulp. Table VII is the result of calculating the data in Table VI to these yields.
Table V

Chemical Composition of Pulps

Original Data

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>0 Hours</th>
<th>½ Hour</th>
<th>1 Hour</th>
<th>2 Hour</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>2.3%</td>
<td>2.1%</td>
<td>2.1%</td>
<td>2.1%</td>
<td>±0.1%</td>
</tr>
<tr>
<td>Lignin</td>
<td>16.0%</td>
<td>18.0%</td>
<td>18.0%</td>
<td>18.0%</td>
<td>±0.5%</td>
</tr>
<tr>
<td>Alpha Cellulose</td>
<td>65.0%</td>
<td>63.5%</td>
<td>64.5%</td>
<td>65.6%</td>
<td>± 1%</td>
</tr>
<tr>
<td>Beta Cellulose</td>
<td>9.3%</td>
<td>9.7%</td>
<td>9.4%</td>
<td>9.1%</td>
<td>±0.4%</td>
</tr>
<tr>
<td>Gamma Cellulose</td>
<td>7.5%</td>
<td>6.0%</td>
<td>5.8%</td>
<td>5.1%</td>
<td>±0.3%</td>
</tr>
<tr>
<td>Total</td>
<td>100.1%</td>
<td>99.3%</td>
<td>99.8%</td>
<td>99.9%</td>
<td>± 1%</td>
</tr>
<tr>
<td>Beta Gamma Cellulose</td>
<td>16.8%</td>
<td>15.7%</td>
<td>15.2%</td>
<td>14.2%</td>
<td>±0.3%</td>
</tr>
<tr>
<td>Lignin Alpha Cellulose Extractives</td>
<td>83.3%</td>
<td>83.6%</td>
<td>84.6%</td>
<td>85.7%</td>
<td>±0.7%</td>
</tr>
<tr>
<td>Yield</td>
<td>64.7%</td>
<td>75.2%</td>
<td>81.2%</td>
<td>±2.5%</td>
<td></td>
</tr>
</tbody>
</table>
Table VI
Chemical Composition of Pulps
Corrected to 100%

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>0 Hours</th>
<th>½ Hour</th>
<th>1 Hour</th>
<th>2 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>2.3%</td>
<td>2.1%</td>
<td>2.1%</td>
<td>2.1%</td>
</tr>
<tr>
<td>Lignin</td>
<td>16.0%</td>
<td>18.1%</td>
<td>18.0%</td>
<td>18.0%</td>
</tr>
<tr>
<td>Alpha Cellulose</td>
<td>64.9%</td>
<td>64.0%</td>
<td>64.7%</td>
<td>65.7%</td>
</tr>
<tr>
<td>Beta Cellulose</td>
<td>9.3%</td>
<td>9.8%</td>
<td>9.4%</td>
<td>9.1%</td>
</tr>
<tr>
<td>Gamma Cellulose</td>
<td>7.5%</td>
<td>6.0%</td>
<td>5.8%</td>
<td>5.1%</td>
</tr>
</tbody>
</table>

Table VII
Chemical Composition of Pulps
Data Applied to the Percent Accepts

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>0 Hours</th>
<th>½ Hour</th>
<th>1 Hour</th>
<th>2 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>2.3%</td>
<td>1.4%</td>
<td>1.6%</td>
<td>1.7%</td>
</tr>
<tr>
<td>Lignin</td>
<td>16.0%</td>
<td>11.7%</td>
<td>13.5%</td>
<td>14.6%</td>
</tr>
<tr>
<td>Alpha Cellulose</td>
<td>64.9%</td>
<td>41.4%</td>
<td>48.6%</td>
<td>53.4%</td>
</tr>
<tr>
<td>Beta Cellulose</td>
<td>9.3%</td>
<td>6.3%</td>
<td>7.1%</td>
<td>7.4%</td>
</tr>
<tr>
<td>Gamma Cellulose</td>
<td>7.5%</td>
<td>3.9%</td>
<td>4.4%</td>
<td>4.1%</td>
</tr>
<tr>
<td>Yield (Total)</td>
<td>100.0%</td>
<td>64.7%</td>
<td>75.2%</td>
<td>81.2%</td>
</tr>
<tr>
<td>Beta plus</td>
<td>16.8%</td>
<td>10.2%</td>
<td>11.5%</td>
<td>11.5%</td>
</tr>
<tr>
<td>Gamma Cellulose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5
Caustic Concentration vs. Pulping Time

![Graph showing caustic concentration vs. pulping time.]

Pulping Time in Hours

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The yield increases with increase in pulping reaction time. Several theories were postulated to explain this. They were: the percent yields were in error, the half hour and two hour cooks had become interchanged, the yields were correct however in the half hour cook a larger amount of pulp had become powdered and consequently passed through the 50 mesh tub screen.

The first theory is disproved when the data is carefully checked and the moisture content of the pulp and chips is rerun. When this was done no significant changes were found.

The second theory was disproved by the fact that the two hour pulp was stronger than the half hour pulp. The zero span factor for the half hour pulp was 4.85, for the one hour pulp 4.78, and for the two hour pulp 5.41 (13). This appears reasonable from the idea that when the chips are pulped longer they become more like chemical pulp and less like groundwood. This is also shown in the literature. Also the amount of gamma and beta plus gamma cellulosomes would show an increase with increase in pulping reaction time if the half hour and the two hour pulps were interchanged (Table VII). This would be very unlikely and would not agree with the literature.

Thus the third theory must be the answer. All literature values show a decrease in yield with increase in pulping reaction time. It is also found that they often determine the yield before the pulp
is refined. In a survey (14) made with pulp in a NSSC cook it was found that if the yield was determined before screening it decreased with increase in cooking time. However if it was made after screening then it was found to increase sharply with cooking time (Figure 6). Thus the third theory must be correct and the yield after screening must increase with increase in cooking time.

The problem arises however that this thesis is mainly concerned with the chemical fractions of the aspen wood and those lost by the reaction with the caustic solution. If the results of the testings are figured upon the yields obtained, then the data will be confusing (Table VII).

The problem is to correct for the fines which were lost in screening. Since the fines which passed through the 50 mesh tub screen flowed directly to the sewer, there was no way of measuring them. Thus the true yield could not be determined by adding up the total accepts plus the large and small rejects.

In order to find a reasonable yield to base the calculations on, the literature was consulted. It was found that Brown and McGovern (1) had made yield determinations under very similar conditions (Table I). They had used two different concentrations of sodium hydroxide, both of which gave the same shape line (Figure 4). Thus to find the theoretical yield a linear interpolation between the two points was made based
Figure 6
Effect of Time on Total and Screened Yield
for NSSC by McGovern
on the sodium hydroxide concentration, liquor to chip ratio and the moisture in the chips. From this information the following yields were obtained; 90.3% for the half hour pulp, 89.2% for the one hour pulp, and 88.7% for the two hour pulp. The difference between these values and the sum of the percent accepts plus large rejects was designated the theoretical small rejects (Table VIII). When the data obtained by the tests were calculated upon the basis of this theoretical yield Table IX was obtained.

**Lignin**

Cold caustic soda pulping does not remove lignin. Figure 7 shows that the amount of lignin remains constant with pulping reaction time. Thus the percent of lignin within each pulp actually increases because other materials are removed (Table VI).

In the cold caustic pulping operation an "artificial lignin" may be formed. Runkel and Schambach (7) in their article pointed out that they suspected the rise of an artificial lignin at higher temperatures (Table VI). Figure 7 shows slightly more lignin after a half hour of pulping reaction time than was started with. In the experiments that Brown and McGovern (1) made with sodium hydroxide concentrations of 63 grams per liter a small increase in the lignin content was also noticed for the half hour pulp (Figure 1). Thus the small increase in lignin for the half hour pulping
### Table VIII

**Yields - Accepts - Rejects**

<table>
<thead>
<tr>
<th>Pulping Time</th>
<th>½ Hour</th>
<th>1 Hour</th>
<th>2 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Accepts</td>
<td>64.7%</td>
<td>75.2%</td>
<td>81.2%</td>
</tr>
<tr>
<td>% Large Rejects</td>
<td>4.8%</td>
<td>4.5%</td>
<td>2.1%</td>
</tr>
<tr>
<td>% Accepts plus Large Rejects</td>
<td>69.5%</td>
<td>79.7%</td>
<td>83.3%</td>
</tr>
<tr>
<td>% Yield (Theoretical)</td>
<td>90.3%</td>
<td>89.2%</td>
<td>88.7%</td>
</tr>
<tr>
<td>% Small Rejects (Theoretical)</td>
<td>20.8%</td>
<td>9.5%</td>
<td>5.4%</td>
</tr>
<tr>
<td>% Total Rejects</td>
<td>25.6%</td>
<td>14.0%</td>
<td>7.5%</td>
</tr>
</tbody>
</table>

### Table IX

**Chemical Composition of Pulps**

Data Applied to Theoretical Yield

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>0 Hour</th>
<th>½ Hour</th>
<th>1 Hour</th>
<th>2 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>2.3%</td>
<td>1.9%</td>
<td>1.9%</td>
<td>1.9%</td>
</tr>
<tr>
<td>Lignin</td>
<td>16.0%</td>
<td>16.3%</td>
<td>16.0%</td>
<td>16.0%</td>
</tr>
<tr>
<td>Alpha Cellulose</td>
<td>64.9%</td>
<td>57.9%</td>
<td>57.7%</td>
<td>58.2%</td>
</tr>
<tr>
<td>Beta Cellulose</td>
<td>9.3%</td>
<td>8.8%</td>
<td>8.4%</td>
<td>8.1%</td>
</tr>
<tr>
<td>Gamma Cellulose</td>
<td>7.5%</td>
<td>5.4%</td>
<td>5.2%</td>
<td>4.5%</td>
</tr>
<tr>
<td>Yield (Total)</td>
<td>100.0%</td>
<td>90.3%</td>
<td>89.2%</td>
<td>88.7%</td>
</tr>
<tr>
<td>Beta plus Gamma Cellulose</td>
<td>16.8%</td>
<td>14.2%</td>
<td>13.6%</td>
<td>12.6%</td>
</tr>
<tr>
<td>Lignin plus Alpha Cellulose</td>
<td>83.2%</td>
<td>76.1%</td>
<td>75.6%</td>
<td>76.1%</td>
</tr>
<tr>
<td>Cellulose plus Extractives</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Figure 7

Lignin vs. Pulping Time

Pulping Time in Hours

Percent
16%
15%
14%
13%
12%
11%
10%
9%
8%
7%
6%
5%
4%
3%
2%
1%
0%
may actually be correct. It may be that more of the lignin is removed but artificial lignin (material which is insoluble in 72% sulfuric acid) is formed to take its place. However there was not enough evidence here to substantiate this theory.

Extractives

The amount of extractives remains about the same during the pulping operation (Figure 8). The alcohol-benzene extractives were obtained mainly to correct the lignin values. The extractives were determined both by the loss in weight of the pulp and the gain in weight of the extraction flask. The loss of weight by the pulp was always greater than the gain in weight by the flask. This may indicate that part of the extractives were volatile. However again there was not enough evidence here to substantiate this theory.

Alpha Cellulose

The pulping reaction time does not effect the amount of alpha cellulose (Figure 9). However during the initial half hour of the reaction time there is a loss of alpha cellulose. This loss was not expected from reviewing the work of Brown and McGovern (1). However their values for alpha cellulose were much lower (Figure 2).

Three theories were purposed to explain this drop in alpha cellulose during the first half hour of the reaction time.
Figure 8
Extractives vs. Pulping Time

Figure 9
Alpha Cellulose vs. Pulping Time
The first theory is that there is an error in the determination of the alpha cellulose. However this can quickly be discounted because two entirely separate tests were made and the values for the two tests were very close.

A second theory is that the refining operations were much more severe for the pulps than for the wood. Therefore the refining operation decreased the amount of alpha cellulose much more in the pulps than in the wood. This theory appears reasonable when it is realized that the pulps were sent through the refiner seven times so that the fibers were separated enough to pass through a ten cut slot screen, while the wood was only put through a hammermill fitted with a coarse screen so that it came out as a fine sawdust.

However if the theory is expanded further it would seem that the two hour cook would have more alpha cellulose than the half hour pulping time because the chips from the two hour pulping reaction were much softer and therefore required much less refining action. But it must also be remembered that the exposure to chemical for a longer period of time may reduce the alpha cellulose. Thus these last two effects may neutralize each other.

Finally there is the theory that the data is correct and some sort of unknown shrinkage of alpha cellulose occurs before it builds up a resistance to the
sodium hydroxide. The literature values do not show this sudden loss. However there was not much information available.

There was not enough information available to support any one of these theories, it is probably a combination of these effects taking place.

Non - Hemicellulose

When the alpha cellulose, lignin, and extractives are summed up and plotted against pulping reaction time, Figure 10 is obtained. This may be considered as the non-hemicellulose fraction of wood. Except for a sudden drop at the beginning because of the alpha cellulose, the graph shows that the non-hemicellulose fraction of wood does not change with the pulping time.

Beta Cellulose

The beta cellulose decreases with increase in pulping time (Figure 11). The decrease in the percent beta cellulose is less between one and two hours than it is between one half and one hour. It appears that if the pulping time were made longer the percent of beta cellulose would eventually become constant.

Beta cellulose might arbitrarily be divided into two parts one which is soluble in five percent sodium hydroxide and one which is not. Thus if it would appear that the fraction of beta cellulose which is soluble in five percent sodium hydroxide would be removed,
Figure 10
Alpha Cellulose plus Lignin plus Extractives vs. Pulping Time

Pulping Time in Hours

Figure 11
Beta Cellulose vs. Pulping Time

Pulping Time in Hours
while that portion not soluble would not change with pulping time. Thus the total beta cellulose content would show a decrease until all of the fraction which is soluble in five percent sodium hydroxide is removed. After this point there would not be any effect on beta cellulose with pulping time.

**Gamma Cellulose**

The gamma cellulose decreases with increase in pulping time (Figure 12). Twenty eight percent of the original gamma cellulose was lost in the first half hour of pulping time. Within two hours forty percent of the original cellulose was removed. From the slope of the line in Figure 12, it could be assumed that with enough time most of the gamma cellulose would be removed. Thus cold soda pulping is in essence a process which removes gamma cellulose.

**Hemicellulose**

The beta cellulose plus the gamma cellulose constitute the hemicellulose. The hemicellulose definitely decreases with increase in pulping time (Figure 13). Over twenty-five percent of the original hemicellulose is removed.

The difference in yield between a half hour pulping time and a two hour pulping time is equal to the amount of hemicellulose dissolved in the pulping liquor (sodium hydroxide). The loss of hemicellulose is
Figure 12
Gamma Cellulose vs. Pulping Time

Figure 13
Beta plus Gamma Cellulose vs. Pulping Time
mainly due to a loss of gamma cellulose and partly due to a loss of beta cellulose.

Only the hemicellulose (beta and gamma cellulose) shows a decrease with increase in pulping time. This shows that the cold soda pulping process is essentially a process which accomplishes its pulping by the removal of part of the hemicellulose rather than by the removal of lignin.
CONCLUSIONS

1. After the first half hour the amount of caustic consumed was proportional to the pulping time.

2. The yield after screening increased with increase in pulping time.

3. The yield before screening decreased with increase in pulping time.

4. Cold soda pulping did not remove any lignin.

5. Alpha cellulose was not removed after the first half hour in cold soda pulping of aspen.

6. Beta cellulose decreased with increase in pulping time.

7. Gamma cellulose decreased with increase in pulping time. Forty percent of the original gamma cellulose was removed in two hours of pulping with five percent sodium hydroxide an aspen wood.

8. The difference in yield between a half hour pulping and a two hour pulping was equal to the amount of hemicellulose (beta plus gamma cellulose) dissolved.

9. The cold soda pulping of aspen is essentially a process which accomplishes its pulping by the removal of part of the hemicellulose (especially the gamma cellulose) rather than by the removal of lignin.
BIBLIOGRAPHY


12. Tappi Standard T 203 m-58
