

KRAFT BORATE LABORATORY COOKS WITH VARYING SULFIDITY

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ABSTRACT

This paper presents the results of a kraft pulping study conducted on western hemlock with white liquor prepared in mill trials using the autocausticizing process. Experiments were performed at 28% and 20% sulfidity levels using both autocausticized and conventional kraft liquors obtained from a pulp mill located in the western United States. The primary conclusion drawn from this work is that for western hemlock at equivalent kappa numbers, the screened pulp yield improved with the use of autocausticized white liquor. At a given kappa number, a higher H-factor was required for the pulp cooked using autocausticized liquor compared to that cooked using the conventional liquor; however, the pulp viscosity and strength were not affected much by the increase in the H-factor, which suggests that borate may protect cellulose fibers from extended damage expected at higher H-factors.

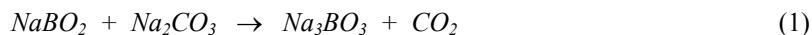
INTRODUCTION

The conventional kraft recovery process involves black liquor evaporation, combustion of black liquor under both reductive and oxidative conditions, smelt dissolution, slaking, causticization, and lime burning (Figure 1). A major drawback to conventional recovery is that two chemical cycles are involved corresponding to a sodium and sulfur cycle and a calcium or lime cycle. The lime cycle increases the complexity of the chemical recovery and leads to high capital cost and an energy penalty due to operation of the lime kiln. Autocausticizing technology involves the use of sodium borate to “causticize” the liquor directly in the smelt dissolving tank following the autocausticizing reaction in the recovery boiler. In principle, the autocausticizing process can eliminate the calcium cycle, thus eliminating the slaking, causticizing, lime kiln, and ancillary unit operations from the recovery cycle.

Autocausticizing Process

Janson and Pekkala at the Finnish Pulp and Paper Research Institute initially developed the autocausticizing technology [1]. Later, the equation for autocausticizing reaction was modified by Tran et al. [2] based on two separate laboratory studies. Based on the work of Tran et. al [2] the borate autocausticizing reactions are given by the following equations.

Autocausticizing reaction in Recovery Boiler



Caustic formation in Smelt Dissolving Tank



The autocausticizing reaction (equation 1) between sodium carbonate Na_2CO_3 and sodium borates is thought to occur at high temperatures in the recovery boiler. The reaction product is believed to be tri-sodium borate, Na_3BO_3 . The reaction kinetics depends upon the sodium-to-boron ratio, temperature, and the concentration of CO_2 in the furnace. The regeneration of caustic is thought to occur in the smelt dissolving tank, where two moles of sodium hydroxide (NaOH) form for each mole of sodium borate ($NaBO_2$) that enters the recovery boiler.

In addition to caustic (NaOH), sodium sulfide (Na₂S) and sodium carbonate (Na₂CO₃), the white liquor obtained from the auto-causticizing process contains borate, which exists mainly as sodium metaborate (NaBO₂) at high pH levels prevailing in the liquor cycle.

Partial auto-causticizing (Figure 2) has recently been performed in a number of mill scale trials [3]. In partial auto-causticizing, only a portion of the NaOH required in the digester comes from the auto-causticizing reaction. The remainder is provided by conventional lime re-causticizing process. The use of partial auto-causticizing is particularly attractive to mills that are limited by the capacity of the lime re-causticizing plant since no lime is required for that portion of the caustic generated in the auto-causticizing process.

Effect of Sulfide Ion in Kraft Pulping

Sulfide ion reacts with water and contributes hydroxide ion used in delignification:



Alkaline hydrolysis reactions reduce the molecular weight of the lignin structures and also remove the methoxyl groups (-O-CH₃) causing formation of phenolate ions. During kraft pulping, the bisulfide ion (SH⁻) participates in the “blocking” reaction and inhibits lignin condensation reactions, impairing the removal of lignin. In essence, bisulfide ion functions as a pulping catalyst and thus speeds up delignification. Pulping at high sulfidity during the kraft process shortens the reaction time compared to pulping with pure sodium hydroxide (soda process) or by pulping at low sulfidity. Thus, the viscosity of the brownstock is higher leaving the digester because of the reduction in pulping time. This elevated viscosity is often preserved across the bleach plant with modern mills that use predominately ClO₂ as the bleaching agent.

Carbohydrate Degradation Reactions

During alkaline pulping, carbohydrate degradation reactions occur by two different pathways -- notably random chain hydrolysis and primary and secondary “peeling” reactions. Random chain cleavage leads to a decrease in molecular weight of the carbohydrates and is seen by a decrease in the intrinsic viscosity of the pulp after dissolution in a suitable solvent. Peeling reactions lead to a decrease in pulp yield and thus raise the cost of the wood going to the pulp mill. Unlike the random hydrolysis reactions, peeling reactions primarily reduce pulp yield but do not significantly affect pulp strength.

Kraft Delignification Using Borate Liquors

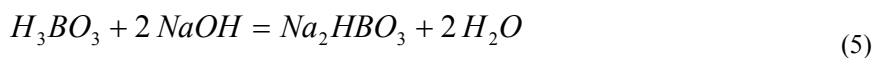
Several authors have conducted kraft pulping studies using synthetic white liquors that contained borate ion. None of these studies, however, were performed using mill white liquor or white liquor produced during mill trials using the auto-causticizing process.

Lowe used sodium tetraborate pentahydrate Na₂B₄O₇•5H₂O, and caustic to simulate sodium metaborate and sodium hydroxide present in the white liquor from the auto-causticizing process [4]. Hemlock chips were pulped using the kraft process with a laboratory simulation of the Extended Modified Continuous Cooking (EMCC) process using regular kraft laboratory-prepared white liquor and an equivalent kraft-borate cooking liquor. Lowe estimated the amount of NaBO₂ and caustic from the following equation.



In these experiments the sulfidity was kept constant at 30%. Lowe (1996) found that the unbleached yield from the EMCC kraft-borate pulping was about 0.6% to 1.3% lower based on wood than EMCC kraft pulping using pure caustic. The kraft-borate cooks required approximately 300 additional H-factor units (hours) to attain the same kappa number. Thus, the viscosities for the kraft-borate brown stocks were 27 to 37% lower than comparable kraft brown stocks.

Similarly, Prihoda, Wandelt and Kubes studied the effects of di-sodium borate on kraft, kraft-AQ and the soda-AQ pulping on black spruce [6]. They measured the alkali requirements, cooking time, pulp yield and pulp quality after pulping with caustic (NaOH) and di-sodium borate (Na₂HBO₃). The di-sodium borate was obtained from boric acid and sodium hydroxide and used as the pulping liquor according to the following reaction:



The presence of borates was found to retard delignification of black spruce in all three processes. The retardation of kraft pulping was compensated by adding anthraquinone, increasing the alkali charge, extending the cooking time, and increasing the cooking temperature. The yield and quality of the pulp was unaffected by the presence of the borates.

Both studies by Lowe et al. [5] and Prihoda et al. [6] were conducted using Janson's autocausticizing formula [1], which assumes one mole of sodium metaborate ($NaBO_2$) is required for each mole of sodium hydroxide ($NaOH$) to achieve 100% autocausticizing in the recovery boiler. According to this formula, the product of autocausticizing reaction in the boiler is di-sodium borate (Na_2HBO_3), which is equivalent to a $NaOH$ to $NaBO_2$ ratio of 1:1. Therefore, the pulping experiments were conducted assuming a similar composition in the white liquor. However, it is proven later that tri-sodium borate (Na_3BO_3), which corresponds to a $NaOH$ to $NaBO_2$ ratio of 2:1, is the actual product of borate autocausticizing reaction in the boiler. In other words, the charge of sodium metaborate in the pulping studies by Janson et al., Lowe et al., and Prihoda et al. was twice as much as that required for borate-kraft pulping at 100% autocausticizing condition. The extra charge of sodium metaborate may have a significant contribution in the lower rate of delignification reported in these experiments and in the low pulp viscosities reported by Lowe et al.

Markham [7] and Gadda [8] report results on the soda oxygen pulping in the presence of borate ion. Markham showed that a borax-oxygen pulping process could improve the pulp yield by 8-9% for mixed hardwoods and up to 12% for spruce as compared to kraft pulp [7]. Since oxygen gas is limited in its solubility and ability to penetrate wood, Markham used poplar wafers of 1.0-mm thickness and spruce wafers of 0.8-mm thickness. Regarding pulp properties, Markham found that pulp produced with borax-oxygen required less energy to refine the pulp to the same freeness as kraft pulp, had higher bulk and lower tear strength. Sodium tetra-borate pulping was found to have several advantages over sodium carbonate as an alkali source for use in oxygen pulping of sliced chips.

Gadda studied the effect of adding sodium perborate on the delignification of pine (*Pinus sylvestris*) fibers during the second stage of a two-stage soda-oxygen pulping process [8]. The process consisted of cooking hand-sorted chips to 65% yield using the conventional soda pulping, disintegrating the partially delignified chips in a refiner and then finish cooking to low lignin content by using a soda-oxygen pulping step at 170°C with 8% $NaOH$ and oxygen at 0.71 MPa. The extent of delignification was estimated by performing UV absorption on transverse sections of fiber to detect the presence of lignin in the secondary wall of fiber. The results showed that the presence of sodium metaborate improved the selectivity of the soda-oxygen delignification reactions. The selectivity was defined as the ratio of the percent delignification and the carbohydrates removed.

OBJECTIVE AND SCOPE

The objective of this work was to determine the pulping characteristics of Northwestern softwood chips with white liquor prepared using partial autocausticizing technology produced in commercial mill trials. Experiments were performed at 28% and 20% sulfidity levels with autocausticized kraft liquor obtained from Mill A where a partial borate autocausticizing process was tested. For the purpose of comparison, control experiments were also performed, at both the 28% and 20% sulfidity levels, using conventional kraft liquor obtained from a nearby sister mill (Mill B) that uses wood from the same wood basket as Mill A. Also, the recovery boiler at Mill A is operated in much the same manner as the recovery boiler at Mill B. Thus, it was thought that the white liquor obtained from Mill B would be quite similar in composition to that obtained from Mill A had it been operating with a conventional recovery boiler. Therefore, the white liquor obtained from Mill B was thought to be representative of white liquor from Mill A had it not been operating with the autocausticizing process. The pulping experiments were conducted under conditions present at Mill A, at 28% and 20% sulfidity to test the theory that it may be possible to pulp with lower sulfidity values and still maintain high brownstock viscosity.

Following the pulping experiments, the response variables were kappa number, screened and total yield, rejects, viscosity, and wet zero span tensile strength. The response variables were plotted against the kappa number and the H-factor, which is a kinetic parameter indicative of the time and temperature in the kraft digester.

EXPERIMENTAL PROCEDURES

Wood Preparation

Softwood chips were obtained from Mill A. Knots and decayed wood were removed prior to screening. The chips were screened in a Weyerhaeuser classifier to obtain a very tight fraction for chip thickness and length. The wood fractions that pass a 1-inch hole but were collected on the 7/8-inch and 5/8 inches round screens were used. These chips were then classified for chip thickness to achieve chips that were less than 10 millimeters thick. The wood was then air dried to a constant moisture level (about 8%) to permit accurate measurement of the mass of wood put into the digester.

Digester Conditions

The baseline conditions used in the pulping experiments are summarized in Table 1 and coincided with the conditions used in Mill A.

Table 1
Kraft Batch Digester Conditions Used in Experimental Cooking

K# centerline	21.0
EA on wood, %	14.0
Baseline sulfidity on TTA	28
Liquor/Wood Ratio	3.6
Nominal Cook Temperature, °F	340
<i>Nominal time to temperature, min</i>	88
<i>Nominal time at temperature, min</i>	55
<i>Causticizing Efficiency, NaOH/(NaOH+Na₂CO₃)</i>	<i>(about 80%)</i>

Experiments at both high (28%) and low (20%) sulfidity conditions were conducted using the above conditions. In conventional kraft cooking, the causticizing efficiency was also specified to determine the Na₂CO₃ concentration in the white liquor. This typically runs about 80% efficiency. The cooking schedule was converted to the H-factor, which was the control parameter used in the pulping experiments by the equation. The H-factor was changed to achieve the entire pulping curve and encompassed the target kappa (permanganate) number used in Mill A.

Mill Pulping Liquors

The white liquor obtained at Mill A had been produced during a partial autoausticizing trial [9], and had approximately 1100 ppm of boron, which was equivalent to about 10% autoausticizing of smelt in the recovery boiler. The mill white liquor was received at the University of Maine and stored under nitrogen to avoid decomposition of the sodium sulfide. The chemical parameters of interest were the total titratable alkali (TTA), active alkali (AA), effective alkali (EA), the sulfidity (S), causticizing efficiency (CE), and activity. The borate white liquor was analyzed using an analytical procedure especially developed by U.S. Borax Inc. that was a variant of the ABC titration. In this method, the boron analysis was performed using inductively coupled plasma spectroscopy as part of a five-point titration procedure to determine the complete analysis of the white liquor.

Conventional pulping liquor obtained from Mill B was analyzed using the ABC titration method. Both samples of pulping liquor were analyzed using plasma spectroscopy to determine the concentration of trace metals. Since the white liquor samples did not contain exactly 28 and 20% sulfidity, sodium sulfide and sodium hydroxide were added to the pulping liquor to achieve the desired high (28%) and low (20%) sulfidity conditions required in the experiments. Using the mill liquors rather than synthetic white liquor ensured that all tramp ions picked up in the recovery cycle from the wood and the piping system are present in the pulping experiments.

Pulping Experiments

Pulping experiments were performed in the University of Maine rocking digester, which holds approximately 2 Kilograms of wood chips for each cook. Kraft control cooks were performed at both the 28% and 20% sulfidity conditions. Five cooks were performed for each pulping condition.

Response Variables

The response variables determined included kappa and permanganate numbers, total yield, screened yield, rejects, 0.5% CED pulp viscosity, wet zero span tensile strength and residual alkali. All response variables were measured using appropriate TAPPI standards.

Analysis of Data

Pulping curves were developed for the kappa number plotted versus the H-factor. Response curves were developed by plotting the total yield, screened yield, rejects, viscosity and wet zero span tensile strength versus the pulp kappa number. Regression lines were put through the response curves and statistical analysis was done by comparing the curves at high and low sulfidity using both pulping liquors.

RESULTS AND DISCUSSION

Composition of White Liquor Samples

Table 2 summarizes the experiments performed in this study while Table 3 shows the results of the chemical analysis of the two samples. The liquor analysis determined at the University agreed with that provided by the mill quite closely; 131 g/l total alkali determined in the mill laboratory and 126 g/l in the UM laboratory. The sample of white liquor obtained from Mill B did not have an analysis. Also, the white liquor sample obtained from Mill B was considerably weaker than the liquor sample obtained from Mill A (see Table 3), only about 91 g/l total alkali compared to the 126 g/l total alkali determined in our laboratory.

Table 2
Summary of Pulping Experiments Performed

Sample	Sulfidity (%)	Effective Alkali (%)	Boron (ppm)
Autocauticize High Sulfidity	28	14	1400
Autocauticize Low Sulfidity	20	14	1400
Conventional High Sulfidity	28	14	6
Conventional Low Sulfidity	20	14	6

(a) Results of UM analysis = 1060 ppm Boron

Table 3
Summary of Chemical Analyses Performed on the Mill White Liquor Samples

	Autocauticized		Conventional
	Mill A	UM	UM
TTA (g/l as Na ₂ O)	130.9	126.3	91.2
AA (g/l as Na ₂ O)	109.3	108.7	83.1
Sulfidity (%)	29.0	30.9	28.3
EA (g/l as Na ₂ O)	90.3	91.9	71.3
Na ₂ CO ₃ (g/l, Na ₂ O)	n.a.	17.5	8.1
Causticizing Efficiency (%)	n.a.	83.2	88.1
Activity (%)	83.5	86.2	91.1
Boron (ppm)	1400	1060	6

Trace Metals Analyses

Table 4 summarizes the trace metal analyses for the two liquors determined using plasma spectroscopy. The data show that the two white liquor samples were very similar in trace elements except for the boron concentration.

There was, of course, a considerably higher value for the boron concentration in the autocausticized white liquor sample (1060 ppm) compared to the conventional white liquor sample (6 ppm) obtained from Mill B. Both of these values were determined at the University of Maine. The boron concentration in the autocausticized liquor sample was also measured at the mill, using a double titration analysis technique developed by U.S. Borax Inc., and reported to be about 1400 ppm (Table 3). Most likely these differences arise from differences in the chemical analysis techniques used in determining the boron content of the liquor.

The aluminum (Al) content in the two white liquor samples averaged between 30 and 40 ppm, while the copper (Cu) and magnesium (Mg) contents in the samples were less than 1 ppm. There was however an appreciable difference in manganese content between the two samples; 2.4 ppm for the autocausticized sample compared to 0.25 ppm for the conventional liquor. Also, because of the lower total alkali in the conventional sample, a lower sodium ion content was measured; 10.1% for the autocausticized white liquor and only 6.82% for the conventional white liquor sample (Table 4).

Table 4
Trace Metal Analysis for Autocausticizing and Conventional Pulping Liquor

White Liquor Samples Concentration (ppm)		
Metals	Autocausticized	Conventional
Al	28	42
B	1060	6
Cu	0.21	0.13
Fe	1.47	0.19
Mg	0.32	0.63
Mn	2.42	0.25
Na	10.1%	6.82%

Response Variables

A comparison was made for the two liquors for each response variable, that is, the kappa number, total and screened yield, rejects, pulp viscosity and wet zero span tensile strength. This was done by plotting the response variables for the high and low sulfidity experiments obtained using the conventional and autocausticized white liquors. The regression equations with the appropriate R^2 values are summarized in Figures 2 through 14. For purpose of comparison, values for the response variables are summarized in Table 5 and 6 for a value of the kappa number of 30 ml. Table 5 compares the response variables as a function of the type of white liquor; that is white liquor prepared using conventional or autocausticizing recovery technology while Table 6 compares the data at the two different sulfidity levels tested.

Table 5
Summary of Pulp Properties at Kappa No. 30
Comparison of Conventional to Autocausticized White Liquor

Sulfidity	20%			28%		
	Conventional Liquor (C)	Autocausticized Liquor (A)	Percent (%) Diff. (A-C)/C	Conventional Liquor (A)	Autocausticized Liquor (C)	Percent (%) Diff. (A-C)/C
H-Factor	2100	2275	8.3	1600	1734	8.4
Total Yield (%)	45.8	45.9	0.2	46.2	46.6	0.9
Screened Yield (%)	43.4	44	1.4	43.3	44.4	2.5
Rejects (%)	2.4	2.0	-16.7	2.9	2.2	-24.1
Viscosity (cps)	36.0	34.8	-3.3	40.5	38.3	-5.4
Wet Tensile (km)	15.3	15.1	-1.3	15.8	15.9	0.6

Table 6
Summary of Pulp Properties at Kappa No. 30 Comparison of 20% and 28% Sulfidity

Sulfidity	Conventional Liquor			Autocausticized Liquor		
	Liquor Type	20% Sulfidity	28% Sulfidity	Percent(%) Diff. (28%S-20%S)/(20%S)	20% Sulfidity	28% Sulfidity
H-Factor	2100	1600	-23.8	2275	1734	-23.8
Total Yield (%)	45.8	46.2	0.9	45.9	46.6	1.5
Screened Yield (%)	43.4	43.3	-0.2	44	44.4	0.9
Rejects (%)	2.4	2.9	20.8	2	2.2	10.0
Viscosity (cps)	36.0	40.5	12.5	34.8	38.3	10.1
Wet Tensile (km)	15.3	15.8	3.3	15.1	15.9	5.3

Kappa Number

Figures 3 and 4 summarize the data for the kappa number plotted against the H-factor used in the cooks. The data in Figures 3 show that within the statistical accuracy of the experiments, the Kappa number versus H-factor curves are virtually the same for cooks performed with the conventional white liquor and the white liquor obtained from Mill A that was practicing partial autoausticizing. From the regression equations, the H-factor required to cook with the conventional liquor would be approximately 8% lower than the H-factor required for the autoausticized liquor. Thus, pulps cooked with the autoausticized white liquor would have slightly higher kappa numbers at a given H-factor than those cooked with conventional kraft liquor.

The effect of sulfidity on kraft pulping is summarized in Figure 4. The data in Figure 4 indicates that increasing the sulfidity of the pulping liquor increases the rate of delignification. At identical H-factor values, pulps cooked at low sulfidity have higher kappa numbers than pulps cooked at high sulfidity. A statistical analysis showed this to be the case for both the conventional white liquor and white liquor prepared by the autoausticizing process (Table 5). From the data in Table 6, the difference in the H-factor required to go to a kappa number 30 between the two white liquor samples was approximately 150 units (Hours), which is low but still significant.

To compensate for this difference, several options are open to the mill to maintain the desired production rate at the desired kappa number. The mill could increase the alkali by a small amount or they could raise the temperature in the digester. A more desirable approach would be to add a small amount of anthraquinone (AQ), typically about 0.05%, to act as a pulping catalyst.

Total Pulp Yield

The data for total (unscreened) pulp yield are summarized in Figures 5 and 6. The autoausticized liquor gave statistically the same pulp yield for the 20% sulfidity case (see Table 6). Figure 5 compares the data for total pulp yield at 28% sulfidity conditions for the conventional and the autoausticized liquors. Figure 6 shows that there is about a 1% increase in pulp yield when the cooking was conducted using the autoausticized liquor at 28% sulfidity. This is reflected in the data for total pulp yield summarized in Table 5.

Figures 6 compares the total pulp yield data for the conditions of high and low sulfidity for the autoausticized pulping liquor. Pulping with the autoausticized white liquor at high sulfidity (28%) gave higher unscreened pulp yield compared to the low sulfidity case (20%). The effect of sulfidity on the unscreened pulp yield was less important for the conventional liquor (Table 6).

Screened Yield

Figures 7 and 8 summarize the data for the screened yield plotted against the kappa number. As the kappa number is lowered, the screened yield invariably decreases. At high kappa numbers, the screened yield will decrease for conventional cook because of increasing rejects.

The results for the screened pulp yield for the conventional kraft liquor is compared to the results for the partially autoausticized white liquor in Figure 7. Statistically, there was higher screened yield for the pulps produced when using the autoausticized white liquor compared to the conventional liquor. This was true for both the high and low

sulfidity conditions, but it was more significant when pulping was done at 28% sulfidity (Figure 7). When pulping with the autocausticized white liquor, the screened yield was higher at low kappa numbers by approximately 1.5 to 2.5%. These results are summarized in Table 5 for pulping to a kappa number of 30.

The screened yield for the high and low sulfidity conditions are summarized in Figure 8 for the partially autocausticized liquor. For the conventional liquor, there was no difference in the screened yield at the high and low sulfidity conditions (Table 6), but there appeared to be a difference for the autocausticized liquor (Figure 8). The bend in the curve for the low sulfidity conditions in Figure 8 at high kappa number reflects the fact that the rejects were high for the low sulfidity cooks at high kappa number.

This is an advantage for pulping with autocausticized white liquor since the cost of wood is a significant fraction of the total manufacturing cost of the pulp. Increased pulp yield is known to occur when reducing agents are added to the pulping liquor. One important additive known to improve pulp yield is sodium borohydride, which acts to reduce aldehyde end groups on the carbohydrates to alcohol groups and limits peeling reactions.

Rejects

Figures 9 and 10 summarize the data for the screened rejects obtained when pulping with the conventional and autocausticized white liquor samples. The data for the rejects were generally lower when pulping with the autocausticized white liquor, especially at kappa numbers below 30 and above 50. This was true for both the high and low sulfidity experiments. Also, when pulping at low sulfidity there were higher rejects, especially at high kappa number. The results can be seen in Table 5, where the data obtained from the regression lines are summarized for kappa number 30.

Pulp Viscosity

The data for pulp viscosity are plotted versus kappa number in Figures 11 and 12. There was little significant difference in the viscosity versus kappa number curves between the two pulping liquors at the low sulfidity level (Table 5). There was about a 5% decrease in viscosity in the pulp produced at the 28% sulfidity level when using the autocausticized white liquor. This was thought to be due to the lower H-factor required with the conventional white liquor. Raising the sulfidity increased the viscosity of the pulp produced with both white liquors. This is shown in Figure 12 for the partially autocausticized white liquor sample. This same behavior also occurred for the conventional kraft liquor. The higher viscosity was thought to be related to the decreased pulping time brought about by the use of high sulfidity levels.

Wet Zero Span Tensile

The data for the wet zero span tensile are summarized in Figures 13 and 14. The wet zero span tensile strength, given as a breaking length, gives similar information to the viscosity test and is an indication of loss of pulp strength that takes place during pulping. Typically, there is more scatter in the wet tensile strength data because sometimes the pulp has kinks and curl that are induced during processing. As the kappa number decreases, the wet tensile strength of the pulp invariably decreases. No statistical difference could be detected in the wet zero span tensile strength between the autocausticized and convention liquors (Figure 13). At the low kappa numbers, the high sulfidity improves the wet strength of the pulp for the autocausticized liquor (Figure 14). Similar results were also found for the conventional white liquors (Table 6).

MILL EXPERIENCE

The partial autocausticizing trial in Mill A lasted over 16 months [9]. While it was not possible to measure the pulp yield and verify the current experimental results during the trial due to the typical noise level in the mill operating data, there was clear evidence of a significant decrease in the black liquor heating value when the boron content of the liquor increased to over 20% autocausticizing. The decrease in the black liquor heating value at 20% autocausticizing was more significant than that expected due to the inorganic load associated with borate in the liquor. This decrease could have been a direct result of the increase in pulp yield, which lowered the organic content of the black liquor and became more evident at the higher autocausticizing levels.

CONCLUSIONS

The primary conclusion drawn from this study is that there is a potential benefit in pulp yield arising from the use of autocausticized white liquor compared to the use of conventional white liquor. Pulping with the autocausticized white liquor resulted in pulp with higher total yield, higher screened yield and lower rejects. At a kappa number of 30, the screened yield was approximately 2.5% higher when pulping with mill produced autocausticized white liquor at 28% sulfidity, when compared to conventional white liquor. Because wood costs are a major contributor to the total cost of the pulp, an increase in pulp yield of 2.5% is quite significant and a major advantage to pulping with the autocausticized white liquor.

To achieve a kappa number of 30, it was determined that pulping with the autocausticized white liquor required approximately an 8% increase in the H-factor when compared to conventional white liquor. This means that at a fixed H-factor and sulfidity, pulp produced using the autocausticized white liquor would have a slightly higher kappa number compared to pulp produced using the conventional liquor. Thus, to achieve a given kappa number, the time in the digester would have to be increased slightly or the temperature would have to be raised. For example, at an H-factor of 1735, pulp produced using the autocausticized white liquor would have a kappa number of approximately 30 while pulp produced using conventional white liquor would have a kappa number of 27.5. The mill could compensate for this small difference in pulping time by adding slightly more alkali, raising the temperature in the digester or by adding a small quantity of antraquinone (AQ) to the pulping liquor.

Since the H-factor was slightly longer, pulping with mill prepared autocausticized white liquor led to a pulp with about 3 to 5% lower viscosity when compared to the pulp produced using conventional mill white liquor. However, this difference in viscosity could not be detected as any appreciable change in wet zero span tensile strength. Since the difference in pulp viscosity between the 20% and 28% levels was small for the autocausticized liquor it should be possible for the mill to lower the sulfidity and still maintain a high viscosity, provided the additional pulping time was acceptable or AQ was added as a pulping catalyst.

Lastly, increasing the sulfidity increased the rate of delignification, reflected in a lower H-factor, higher pulp yield and higher pulp viscosity at a given kappa number. This was true for both the conventional white liquor and the autocausticized white liquor.

While a higher H-factor to a target kappa number typically results in a lower pulp yield and lower pulp viscosity and strength (e.g. when the sulfidity decreases), the increase in H-factor for the partial autocausticizing liquor resulted in a higher pulp yield. The pulp viscosity decreased but not to the extent expected with the increase in H-factor. The Wet Zero Span tensile strength was the same at the low kappa number values and slightly better for the autocausticized liquor at higher kappa numbers. This suggests that borate may protect the cellulose fibers from extended damage during the higher H-factor pulping, and hence increase the pulp yield and decrease the effect on pulp viscosity and strength. In fact, no need was experienced to increase the H-factor in the operation of the batch digesters, and no change was observed in the pulp viscosity and strength during the partial autocausticizing trial in Mill A [9].

Thus, based upon the results presented here for kraft pulping with mill liquors, it is concluded that the autocausticized white liquor is at least as effective as the conventional mill white liquor, and holds the potential for improving pulp yield.

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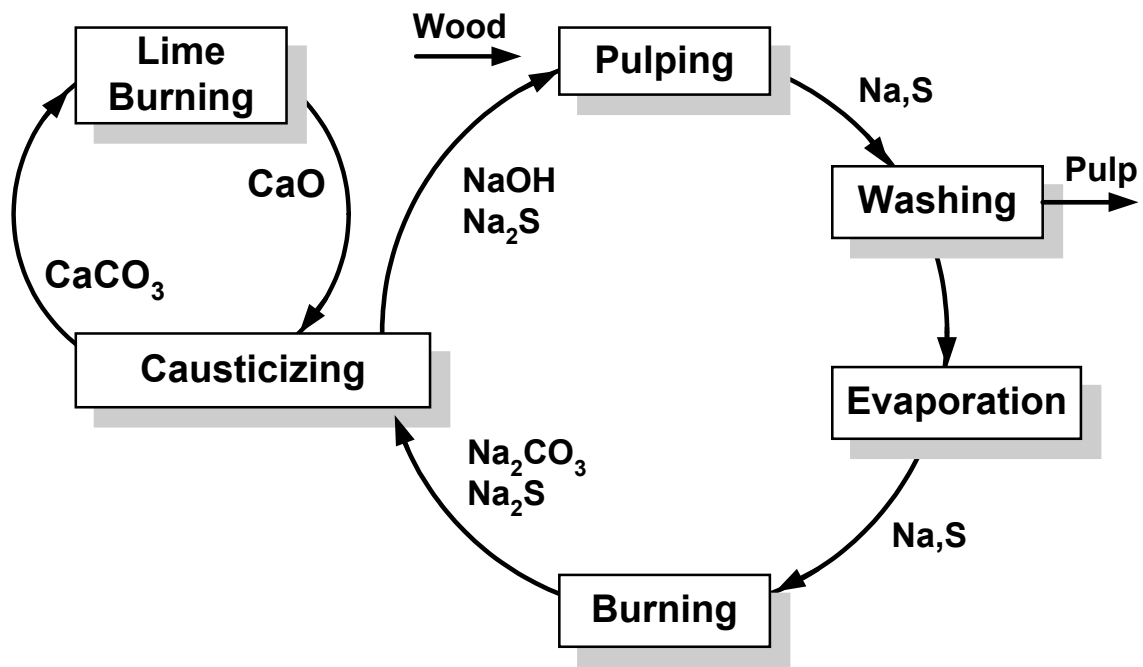


Figure 1. Conventional Kraft Recovery Process

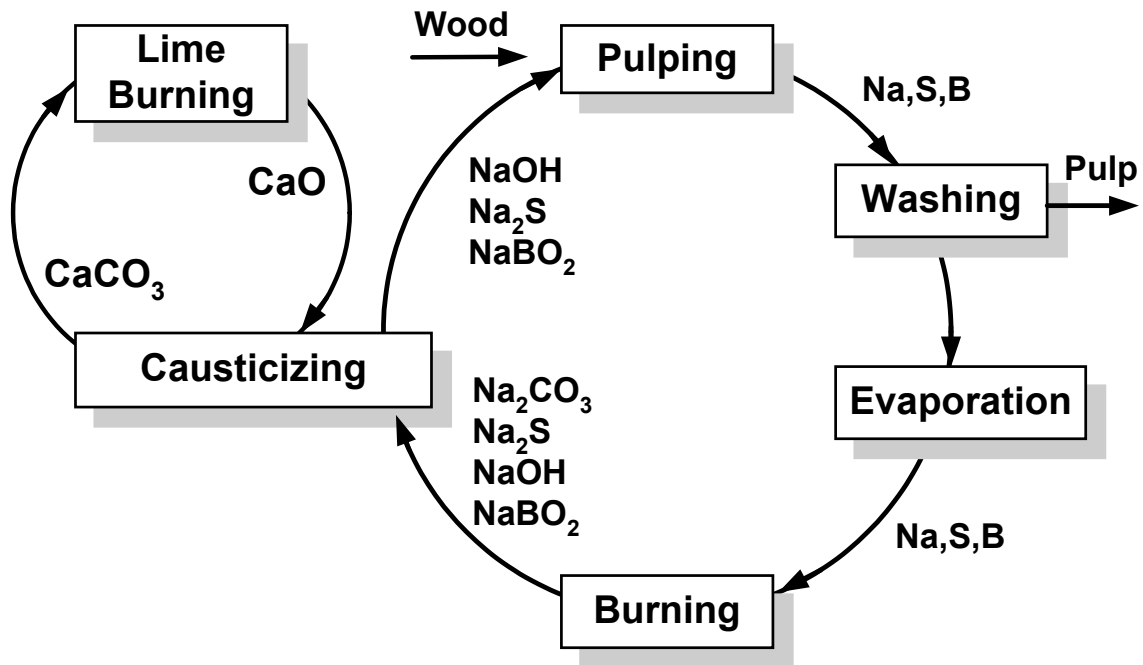


Figure 2. Partial Borate Autocausticizing

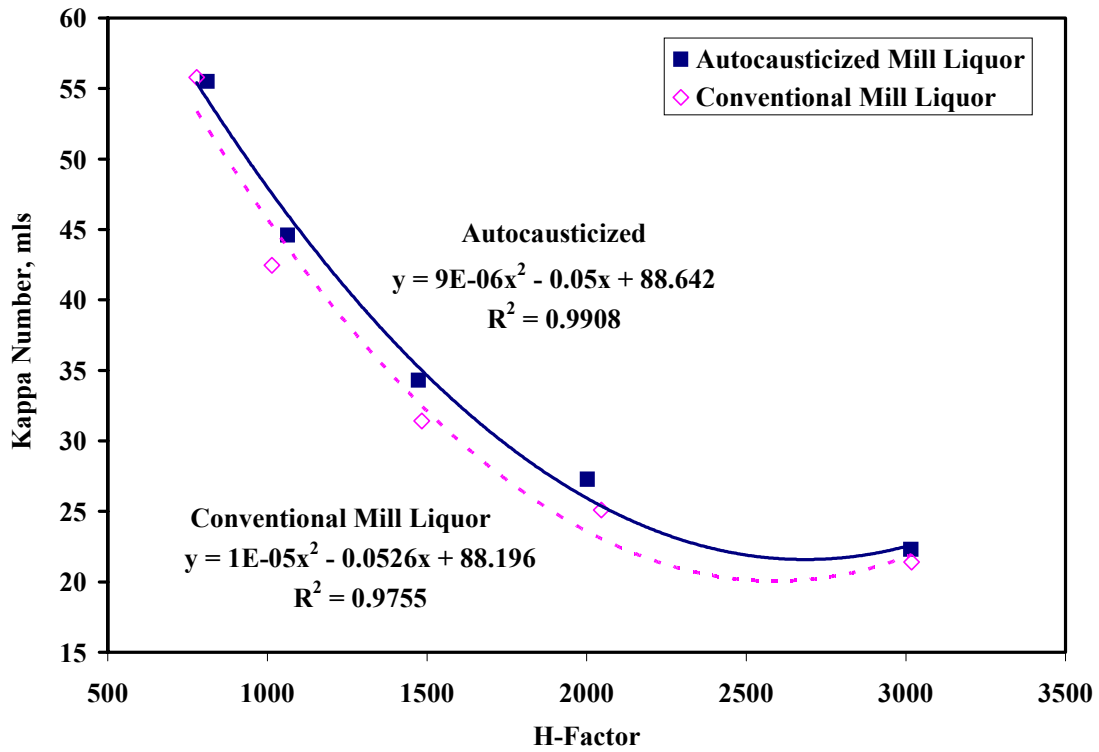


Figure 3. Kappa Number at High Sulfidity (28%) - Conventional and Autocausticized White Liquors

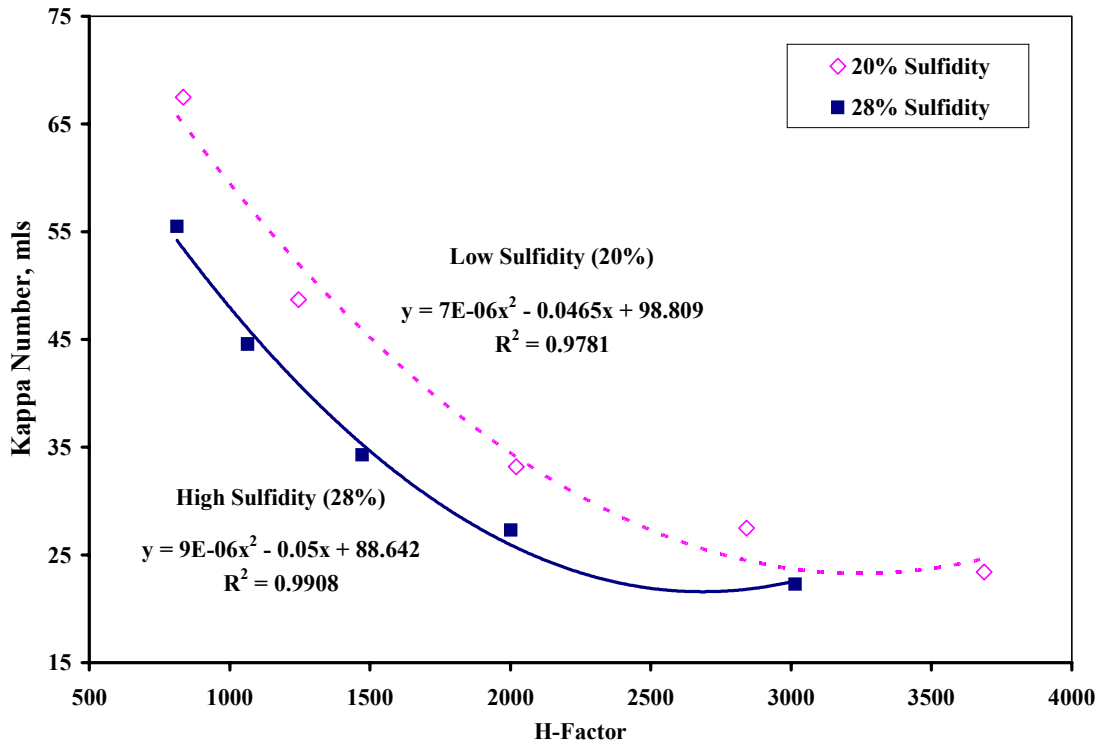


Figure 4. Effect of Sulfidity on Kappa Number Obtained-Using Autocausticized Mill Liquor

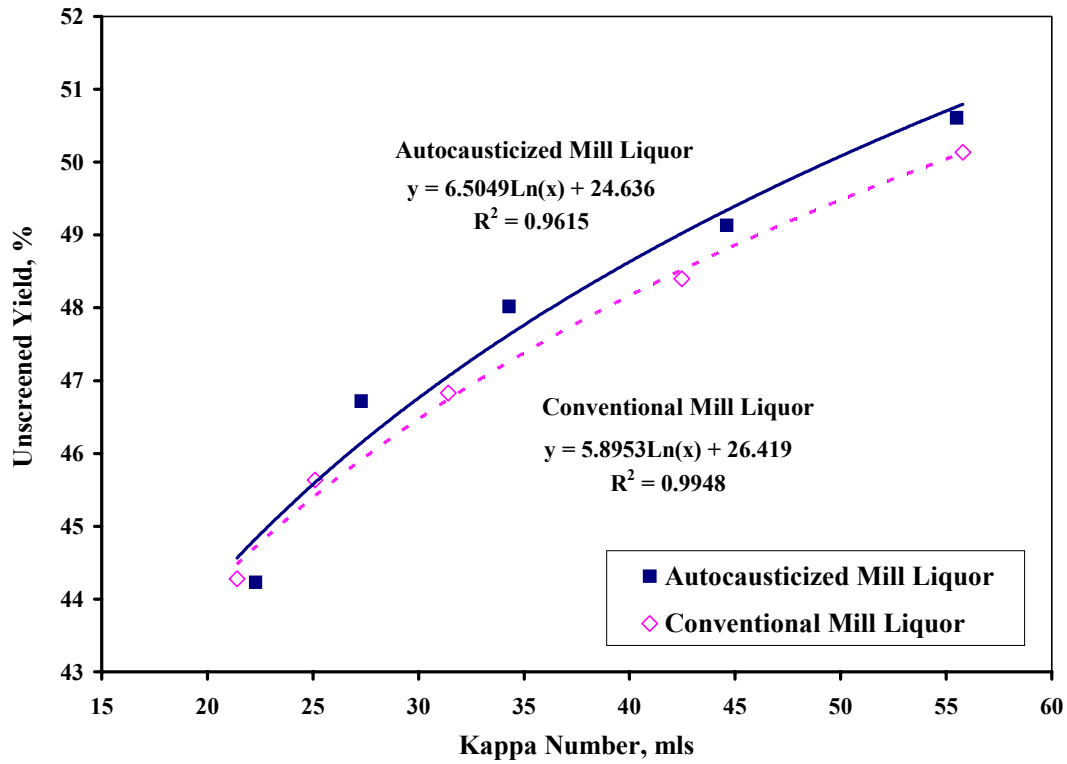


Figure 5. Total Pulp Yield at High Sulfidity (28%)-Conventional versus Autocausticized White Liquors

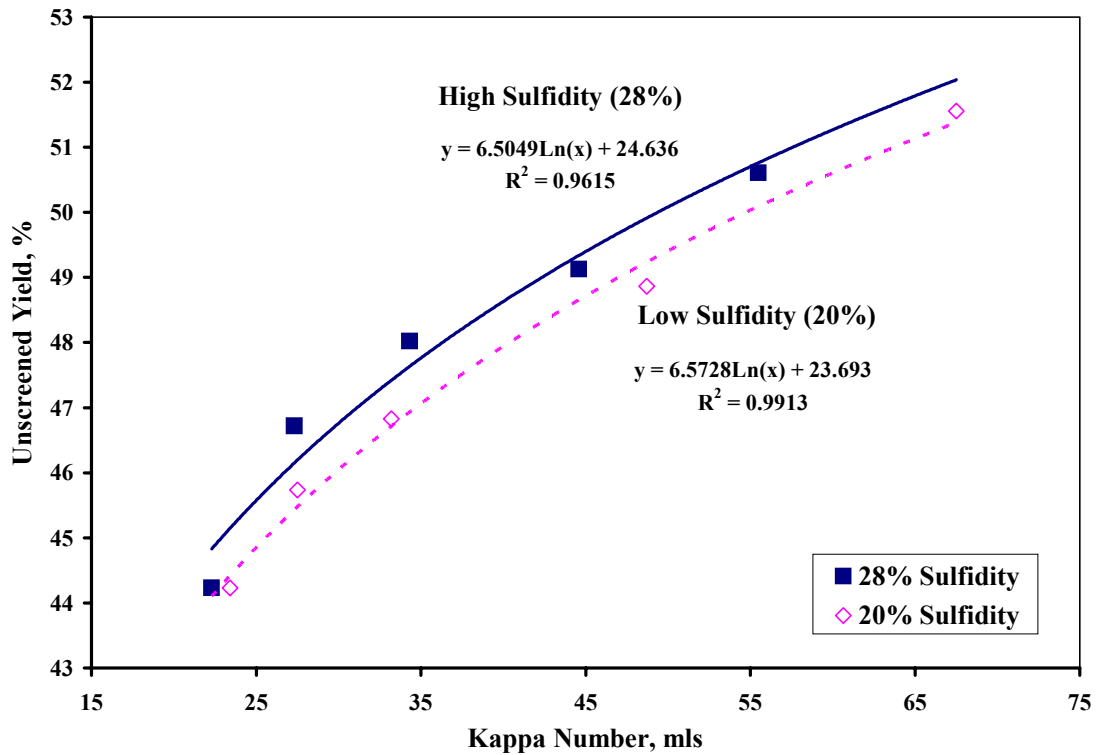


Figure 6. Effect of Sulfidity on Total Pulp Yield Obtained-Using Autocausticized Mill Liquor

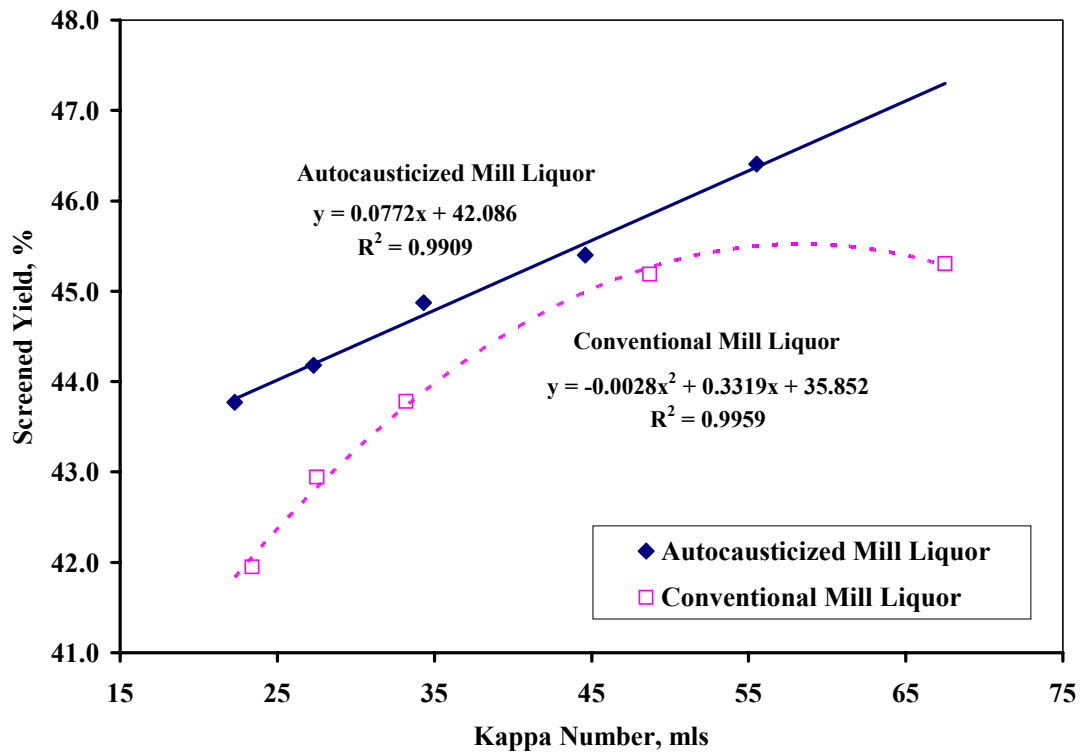


Figure 7. Screened Pulp Yield at High Sulfidity (28%)-Conventional versus Autocausticized White Liquors

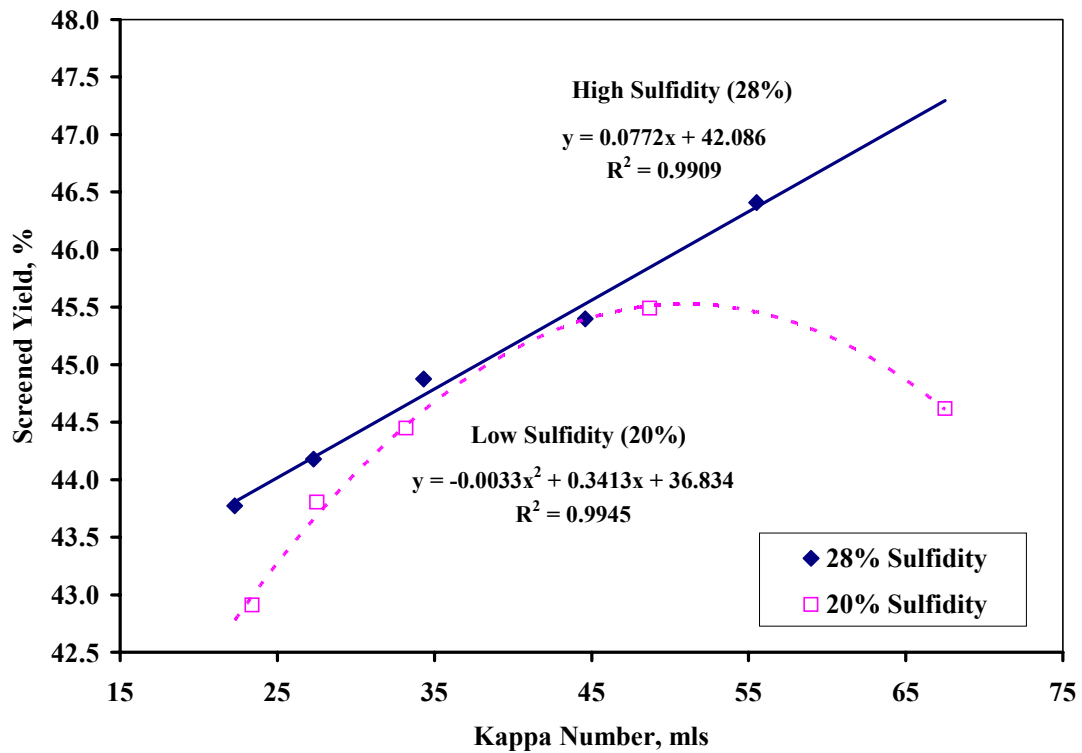


Figure 8. Effect of Sulfidity on Screened Pulp Yield Obtained-Using Autocausticized Mill Liquor

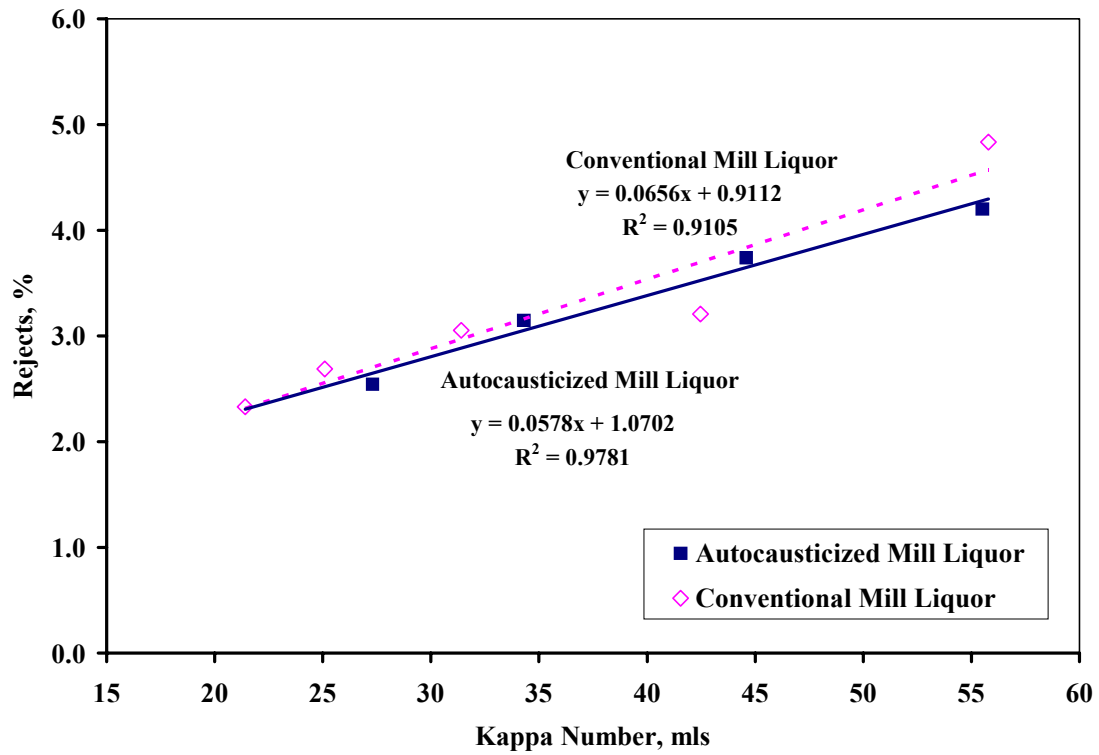


Figure 9. Rejects at High Sulfidity (28%)-Conventional versus Autocausticized White Liquors

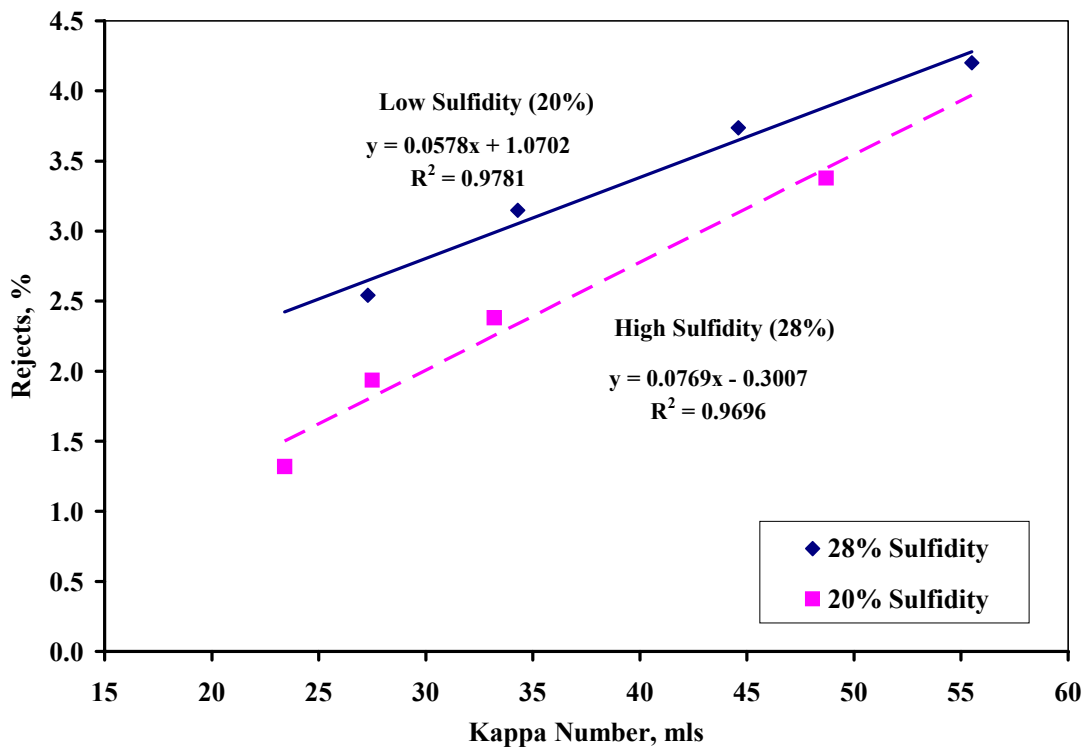


Figure 10. Effect of Sulfidity on Rejects Obtained-Using Autocausticized Mill Liquor

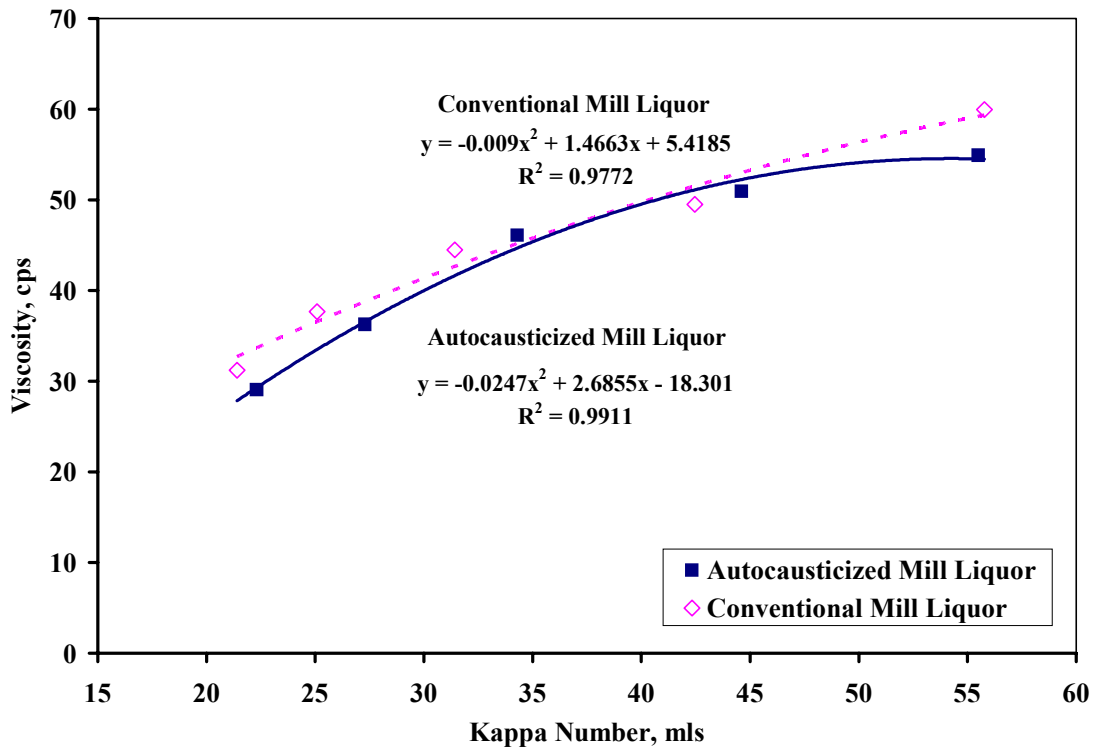


Figure 11. Pulp Viscosity at High Sulfidity (28%)-Conventional versus Autocausticized White Liquors

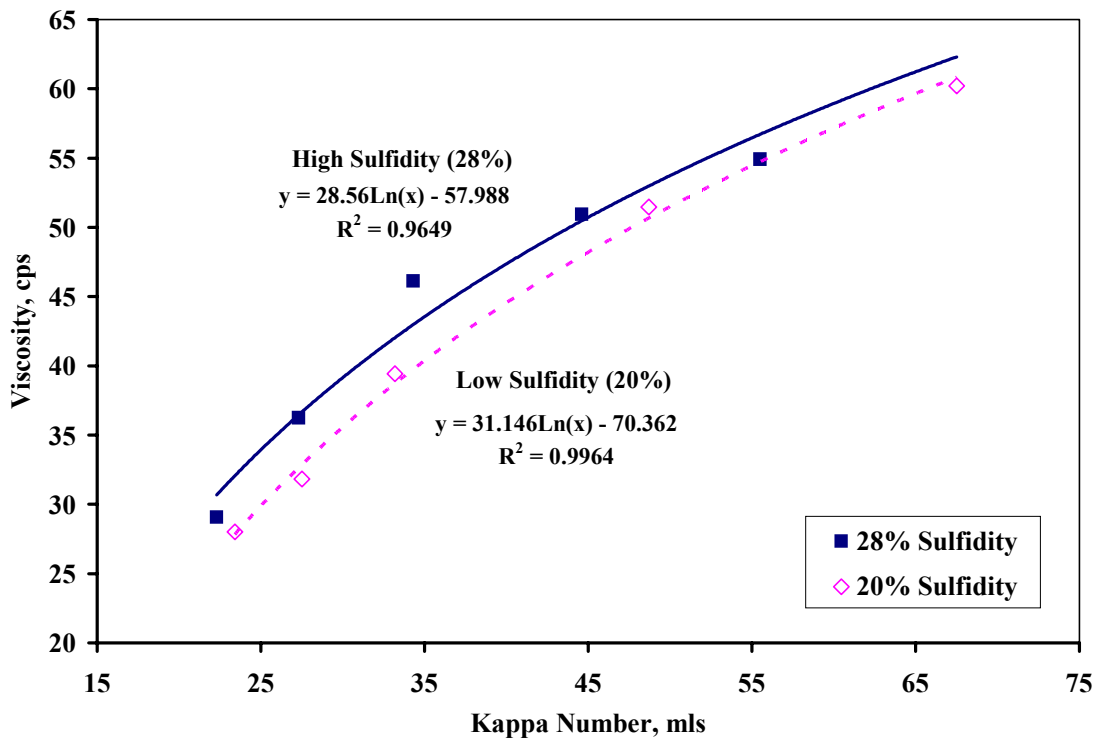


Figure 12. Effect of Sulfidity on Pulp Viscosity Obtained-Using Autocausticized Mill Liquor

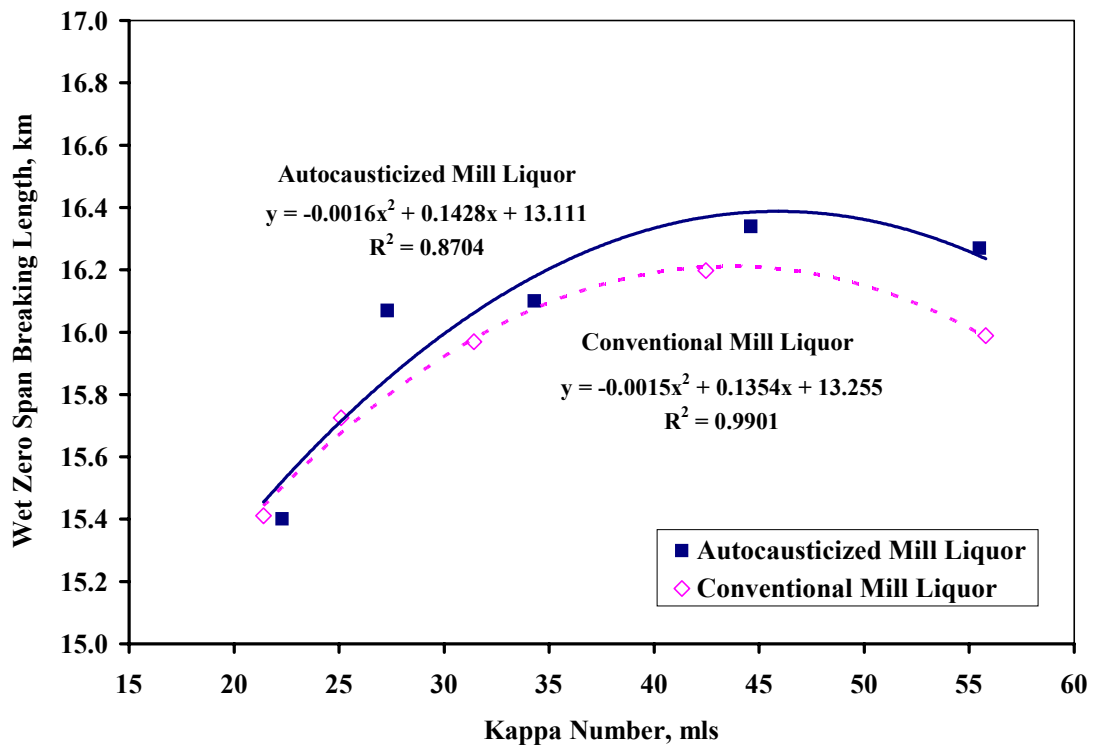


Figure 13. Wet Tensile at High Sulfidity (28%)-Conventional versus Autocausticized White Liquors

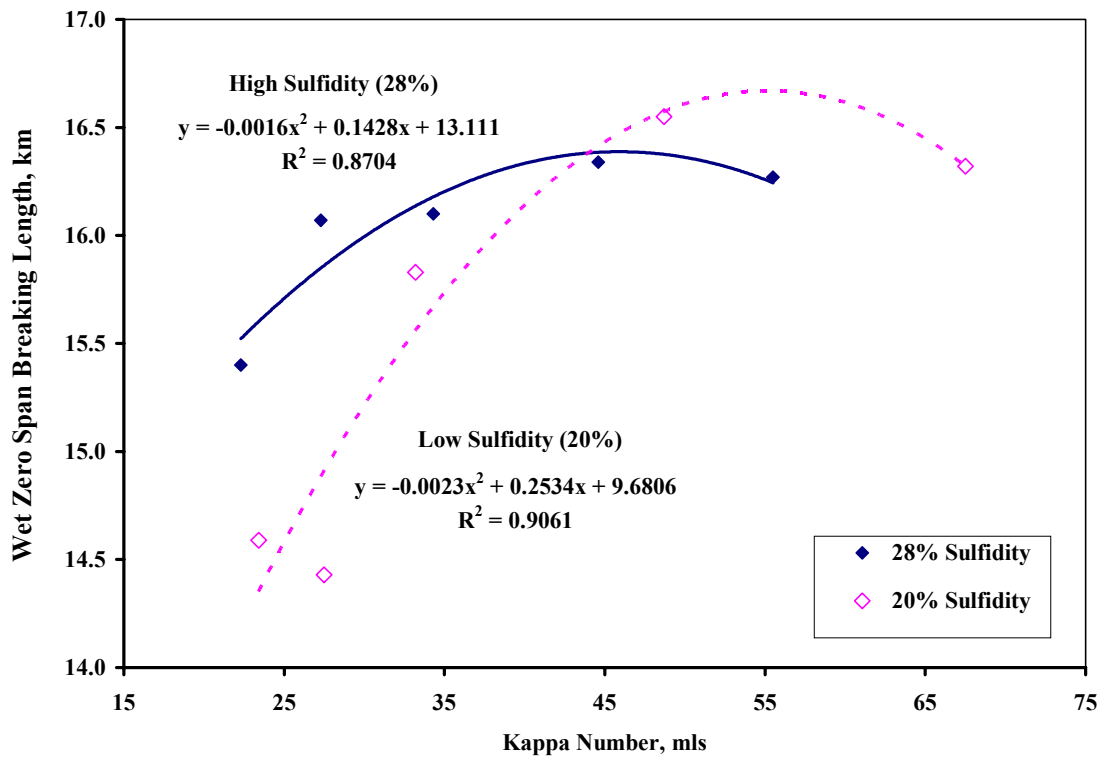


Figure 14. Effect of Sulfidity on Wet Tensile Obtained-Using Autocausticized Mill Liquor