The Influence of Different Types of Bisulfite Cooking Liquors on Pine Wood Components

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In this laboratory study, the initial phase of a single-stage sodium bisulfite cook was observed and analyzed. The experiments were carried out using either a lab- or a mill-prepared cooking acid, and the cooking temperature used in these experiments was 154 °C. Investigated parameters were the chemical consumption, the pH profile, and the pulp yield with respect to cellulose, lignin, glucomannan, xylan, and finally extractives. Cooking was extended down to approximately 60% pulp yield and the pulp composition during the cook, with respect to carbohydrates and lignin, was summarized in a kinetic model. The mill-prepared cooking acid had a higher COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) content than the lab-prepared cooking acid and this influenced the pH and the formation of thiosulfate during the cook. It was found that the presence of dissolved carbohydrates and lignin in the bisulfite cooking liquor affected the extractives removal and the thiosulfate formation.

Keywords: Bisulfite pulping; Cellulose; Extractives; Glucomannan; Kinetics; Lignin; Pine; Sulfate; Thiosulfate; Xylan

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INTRODUCTION

The sulfite pulping process was developed by B. C. Tilgman in 1866-1867, using calcium as the base to manufacture paper pulp from wood (Rydholm 1965; Sixta 2006). The first sulfite mill was started in Bergvik, Sweden in 1874, using magnesium as the base (Sjöström 1993). The sulfite process employs various cooking bases, such as calcium, magnesium, sodium, and ammonia. It also offers a wide range of operating pH levels, ranging from highly acidic to highly alkaline conditions. Until the 1930s, calcium was the base typically used with sulfurous acid. However, magnesium has recently become the dominant sulfite cooking agent. This trend can be attributed to the more beneficial chemical and heat recovery systems involved (Hoge 1954; Annergren and Germgård 2014).

During a sulfite cook, there are beneficial reactions that delignify the pulp, as well as several unwanted reactions that decompose the cooking chemicals or react with the cellulose and/or the hemicellulose (Annergren *et al*. 1960, 1961; Rydholm 1965). In sulfite pulping, the dissolution of lignin is initiated by the sulfonation of lignin, which forms solid lignosulfonic acid (Rydholm and Lagergren 1959). The solid lignosulfonic acid is rendered soluble by a hydrolysis reaction in the later part of the cook and is consequently removed from the wood (Wenzl 1970). During sulfonation, a large number of sulfonate groups are attached to lignin side chains, and the complete sulfonation of all lignin units takes place within a few hours of the sulfite pulping process (Sarkanen and Ludwig 1971). The formation of thiosulfate and sulfate during sulfite pulping can be used as an indicator as to the extent of unwanted reactions. However, if the pulping conditions also lead to a low content of cooking chemicals (especially a low content of "combined SO_2"), there is a high risk for lignin condensation reactions at the end of the cook (Sixta 2006). In the worst case scenario, this can lead to a black cook, where the pulp is rendered useless because of a high degree of lignin condensation reactions (Kaufmann 1951). Detailed studies on the cooking chemistry and the formation of thiosulfate and sulfate during the cook were carried out in the 1960s by Schöön (1962) and Sjöström *et al.* (1962).

The objective of the present study was to investigate the initial phase of bisulfite cooking of pine with respect to the dissolution of different wood components, as well as inorganic and organic side reactions. The study was also focused on the difference in the cooking reaction when two different types of bisulfite cooking acids were used; one was mill-prepared, and the other was lab-prepared. The mill-prepared cooking acid had high COD (Chemical Oxygen Demand) and TOC (Total Organic Carbon) contents and was collected from a Swedish sulfite pulp mill. The high COD and TOC content in the mill cooking acid was due not only to the presence of dissolved lignin and carbohydrates, but also due to the presence of organic acids, extractives, and a small amount of inorganic compounds generated in earlier cooking cycles. The lab-prepared cooking acid had very low COD and TOC values, showing that the lab cooking acid contained only inorganic components.

EXPERIMENTAL

Materials

Pine chips were collected from a Swedish sulfite pulp mill. They were screened and classified in a standard chip classifier. The chip classifier had a series of trays (Ø45 mm, // 8 mm, Ø13 mm, Ø7 mm, Ø3 mm, and < Ø3 mm), and chips that remained on the 13-mm tray were used for the experimental trials ("Ø" represents holes of certain diameter and "//" represents the slots of certain width). The knots and chips with bark were manually removed. The acceptable chips were frozen and stored until use in the cooking experiments.

The mill-prepared bisulfite cooking acid was collected from the same pulp mill, and its composition is given in Table 1. However, in the majority of the experiments, a lab bisulfite cooking acid was used, and its composition is also given in Table 1. The starting pH of the cooking liquor used for the bisulfite cooking experiments was 4.5, measured at room temperature. The cooking experiment procedure is also described in Deshpande *et al.* (2014, 2015).

Cooking Liquor Preparation

The sulfite cooking acid was prepared by adding NaOH into distilled water and then slowly agitating the mixture until it was completely dissolved. After dissolution of sodium hydroxide, SO_2 gas was passed through the solution (with slow agitation) until a constant pH reading of 4.5 was obtained. The sulfite cooking liquors were analyzed for total SO_2 content, free SO_2, and combined SO_2, determined by an iodometric titration, followed by another titration with $Na_2S_2O_3$. The total SO_2 summarizes the content of SO_2, HSO_3^-, and SO_3^{2-} . The so-called combined SO_2 value is a measure of the amount of cation ("base") in the system and is defined as the amount of SO_2 that is needed to produce XSO_3 or X_2SO_3, where X is the cation, *i.e.*, Ca^{2+}, Mg^{2+}, Na^+, or NH_4^+. The free SO_2 is approximately the difference between the total SO_2 and the combined SO_2. The composition of the respective cooking liquors is shown in Table 1.

Table 1. Initial Composition of the Two Cooking Acids Used in the Experiments

	The mill prepared cooking acid	**The lab prepared cooking acid**
COD, (g/L)	49	5
TOC (g/L)	18.5	0
Total SO_2 (%)	2.7	2.7
Combined SO_2 (%)	1.5	1.5
Free SO_2 (%)	1.2	1.2
$Na_2S_2O_3$ (g/L)	0.8	0
Na_2SO_4 (g/L)	3	0
pH	4.5	4.5
Base (% of wood and calculated as Na_2O)	5	5

Cooking Procedure

The cooking experiments were carried out in a lab digester with six autoclaves, each with 1-L capacity. The initial amount of chips in each autoclave was 100 g, calculated as oven-dry material. The autoclaves rotated slowly in a glycol bath, whereby they were heated according to a predetermined temperature profile, shown in Fig. 1. The startup temperature was 100 °C and the L/W-ratio was 4.6. The temperature was raised 1 °C /min to an intermediate temperature, after which the temperature was raised again for 1 h up until the final cooking temperature was achieved. Note that time zero was defined as the time when the full cooking temperature was reached. In other words, it was the time when the autoclaves were negatively mounted into the digester. In this case, it was minus 2 h, as shown in Fig. 1.

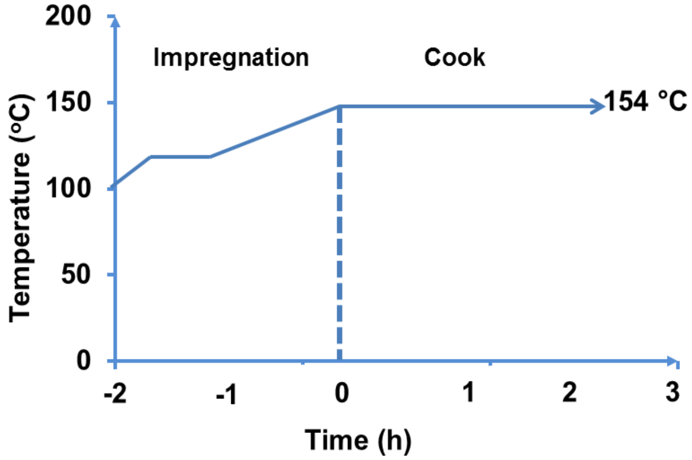

Fig. 1. The temperature profile during the laboratory experiments. The L/W-ratio was always 4.6, and the final cooking temperature was 154 °C.

Analysis Methods

At the end of each cook, the autoclaves were cooled rapidly after being submerged into cold water (approximately 10 °C) to prevent further reactions. Pulp and liquor samples were then collected. The pulp samples obtained after cooking were collected in a sieved basket with a volume of 5 L and with a mesh size of 80. All the pulp samples were washed at the same time in a tank of about 40 L capacity. Washing was carried out during 15 h with distilled water of room temperature and the washings were done in wash cycles, where the wash water level would raise and decrease continuously. The wash water flow rate was 1 L/minute, corresponding to approximately 2 m^3/ ton of pulp for the whole 15-h wash. The washed pulp samples were dried at 45 °C to air-dried equilibrium conditions. After drying, the pulp samples were ground in a Wiley mill to obtain a fine powder, which was passed through a 0.4-mm mesh screen (40 mesh), and these powder samples were used to analyze the various pulp components, as described in Table 2.

Table 2. Testing Methods used for the Wood and Pulp Samples

Acetone extract	ISO 14453
Klason lignin	TAPPI T-UM 250 (1985)
Lignin (UV)	TAPPI T 222 (1988)
Arabinose, Galactose, Glucose, Mannose and Xylose	SCAN-CM 71:09 *
Total-S	SCAN-CM 57
*Calculated as anhydrous sugar	

The spent cooking liquors were analyzed, and the results are shown in Table 3. The composition of the pulp was based on acetone-extracted pulp samples. The carbohydrate monomer values and weights were recalculated to the initial carbohydrate polymers, using the correlations of Meier (1958). Thus, cellulose, glucomannan, and xylan were calculated using the following equations (Eqs. 1 to 3):

$$Cellulose = Glucose - Mannose/3.5 \tag{1}$$

$$Glucomannan = Mannose \times (1+1/3.5) + Galactose \tag{2}$$

$$Xylan = Xylose + Arabinose \tag{3}$$

However, when analyzing the carbohydrates, there is a significant fraction of the pulp that does not dissolve, and it is therefore reported as “residual,” which is at least 10%, but in some cases 20% to 30%, of the bone dry pulp weight. Some laboratories do not report this amount at all, as it does not respond to the carbohydrate test and is therefore considered to be “something else,” although it is well-known that wood and pulp consists only of lignin and carbohydrates. Secondly, when analyzing the carbohydrate monomers the results can be reported as with or without the presence of one water molecule per glucose unit. This water amount has in this study been subtracted, and we likewise have not included the residual in the carbohydrate analysis, which means that our numbers for cellulose, glucomannan, and xylan are on the low side when compared to historic figures reported in, for example different text books like Rydholm (1965). In our study all the carbohydrate monomers are calculated as anhydrous glucose monomers.

Table 3. Testing Methods used for Spent Liquors

Sulfate	SCAN-N 36
Lignin	TAPPI T-UM 250 (1985)
Sulfite	SCAN-N 36
Thiosulfate	SCAN-N 36
Total-S	SCAN-N 35
COD	SS 028142-2
TOC	ISO 8245

The final pulp sample evaluation was done according to the correlation “$\ln W_i = a \text{ x } t + b$,” where “$\ln W_i$” is the logarithm of the parameter “W_i.” This general equation is the integrated version of a first-order reaction, where “a” is a constant at a given chemical composition, “b” is a second constant, and “t” is the cooking time. Because of the non-constant cooking chemical concentrations during the pulping reactions, the kinetic data evaluation had to be based on the initial phase of the stage.

RESULTS AND DISCUSSION

Cooking pine using sodium bisulfite and the addition of cooking acid at pH 4.5 was carried out using lab- and mill-prepared cooking acid. The latter was collected from a Swedish sodium sulfite pulp mill. The chemical compositions of the cooking acids are presented in Table 1, and the cooking temperature profile during a cooking cycle is shown in Fig. 1. The final cooking temperature was 154 °C.

The effect of cooking time on the total cooking chemical consumption, as well as the side reactions with respect to thiosulfate formation are shown in Fig. 2. Thus, the chemical consumption was higher when the mill acid was used compared with the lab acid, indicating a higher reaction rate for the mill acid cook. The higher chemical consumption rate for the mill acid cook may be due to the high COD content in the cooking liquor. Thiosulfate formation during sulfite pulping is an indication of side reactions, which are detrimental to the cooking efficiency. Thiosulfate reacts with the sulfonatable groups of lignin, causing prior phenolation of lignin, and retarding lignin dissolution. This thiosulfate reaction with lignin results in lignin condensation reactions, and if left uncontrolled, will produce a black cook (Kaufmann 1951; Hoge 1954). The thiosulfate content in the cooking liquor increased when lab-prepared cooking acid was used compared with mill-prepared acid. The reason for the significantly higher thiosulfate contents in the cooking experiments compared with the lab-prepared cooking acids can be explained as being a result of the difference in the lignin and carbohydrate contents in the two types of cooking acids. It is well known that thiosulfate is formed in chemical reactions between the bisulfite ions and the reducing end groups in cellulose and hemicellulose (Schöön 1962; Sixta 2006), and it is also well-known that thiosulfate can be formed in the liquor phase when bisulfite reacts with dissolved glucose monomers (Schöön 1962). However, in a mill cooking acid case there was dissolved lignin present and earlier investigations by many researchers have revealed that thiosulfate ions and lignin can react to form thioethers (Sjöström 1993; Goliath and Lindgren 1961); which can later result in problematic lignin condensation reactions. Thus the lignin content in the liquor phase acts as a thiosulfate remover from the liquor phase. In the lab-prepared cooking acid, the lignin content was zero and the thiosulfate thus formed was not removed in lignin reactions; its concentration in the liquor phase therefore could be assumed to be higher than if a mill-prepared cooking acid was used. The correlations between the total SO_2 consumption and the thiosulfate formation show that part of the bisulfite ions in the lab acid were consumed in side reactions to form thiosulfate. From the figure, it can be seen that the cooking chemicals were completely consumed after 5 h of cooking time in both cases, and if the cook had been carried out beyond this point, then lignin condensation reactions would have been favored, according to Kaufmann (1951).

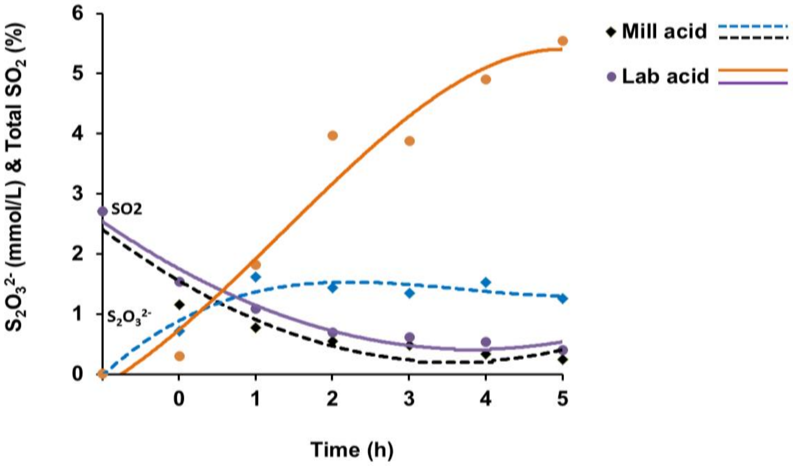

Fig. 2. Influence of cooking time on the total SO_2 consumption and thiosulfate formation during the bisulfite cooking of pine. Conditions used: temperature 154 °C**,** 2.7% total SO_2, and 1.5% combined SO_2, calculated as SO_2. The cooking acid used in this case was either mill-prepared or lab-prepared cooking acid with an initial pH of 4.5. The sodium base charge was 5% of wood, calculated as Na_2O.

No difference was detected in the cellulose content after bisulfite cooking (up to 5 h) for either lab or mill cooking acid, as shown in Fig. 3.

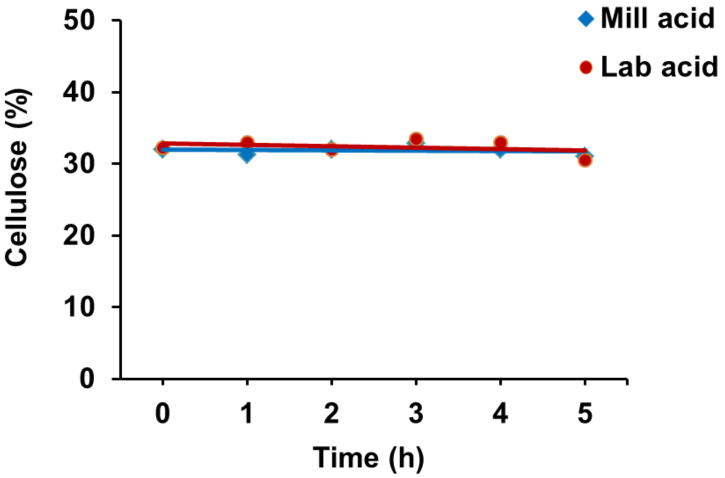

Fig. 3. The effect of time on the cellulose content during bisulfite cooking of pine. Conditions used

were the same as Fig. 2. Two types of cooking acids were used.

Therefore, there was no cellulose degradation during the initial phase of the cook. This is in accordance with earlier studies by Sjöström *et al.* (1962) and Meier (1962), who showed that the cellulose yield is not affected during bisulfite cooking until the pulp yield drops below 50%. Cellulose is more orderly structured than hemicelluloses and is highly polymerized in nature, with a high degree of crystallinity. The highly crystalline nature of cellulose makes it less susceptible to acidic hydrolysis, unless the delignification is extended to very low lignin content and it is subjected to rather drastic cooking conditions (Sjöström 1993). The final pulp yield in both the mill- and lab-prepared cooking acid cases was above 60% after 5 h of cooking time.

The glucomannan and xylan removal during bisulfite cooking with mill-prepared and lab-prepared acid is shown in Fig. 4. The initial glucomannan and xylan removal rates were higher in the cooking experiments when a mill acid was used. The higher reactivity for the mill acid cook may be due to a more stable pH during the cook in comparison with the lab-prepared acid. From the graph, it can be seen that the glucomannan and xylan removal took place continuously throughout the 5 h of cooking time. There was no noticeable difference in the glucomannan removal rate between the mill and the lab acids, from 0 h to 5 h cooking time, and the same phenomenon was observed for the xylan removal rate as well. It can be concluded that the mill acid had an influence on the hemicellulose removal only in the initial phase of the cook, after which there was no major difference in hemicelluloses removal when mill or lab acid was used in the cooking experiments. The reduction in the hemicellulose content during bisulfite cooking (as shown in Fig. 4) has also been previously reported by Annergren (1960, 1961) and Rydholm (1965).

The hemicelluloses are less structured and have a lower degree of polymerization compared with cellulose, and are therefore to a large degree removed during bisulfite cooking (Annergren and Rydholm 1959; Rydholm 1965; Sjöström 1993). It is also known that glucomannan is somewhat more resistant to acidic degradation than xylan, but a substantial amount of glucomannan is dissolved during acid bisulfite cooking (Wenzl 1970; Ingruber *et al.* 1993). Xylan is subjected to major hydrolytic degradation during bisulfite cooking; it is dissolved in spent liquor and is present as xylose sugars (Ingruber *et al.* 1993).

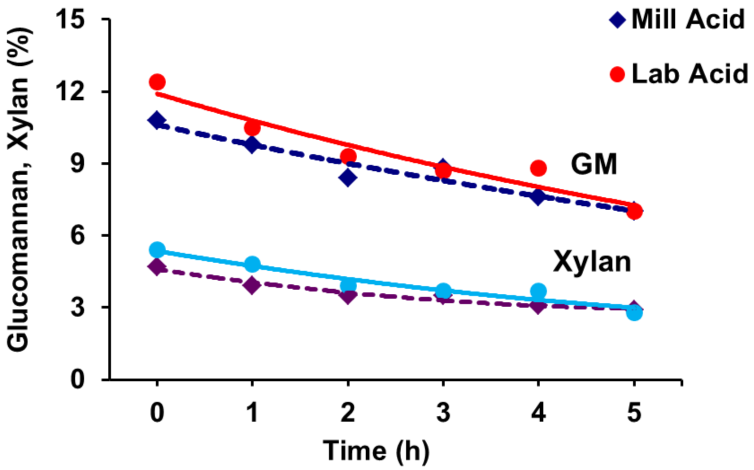

Fig. 4. The influence of cooking time on glucomannan and xylan removal during the bisulfite

cooking of pine. Conditions used were the same as in Fig. 2.

The correlations for yield, lignin, glucomannan, and xylan in the pulp using a lab cooking acid have been summarized in Table 4, using Eq. 4,

$$\ln W_i = a\,t + b \tag{4}$$

where W_i is the content of component i, a and b are constants, and t is the cooking time (see Experimental section). Note that time zero was defined as the time when the full cooking temperature was reached, meaning the time when the autoclaves were mounted into the digester was negative, in this case minus 2 h. The equation can, for example, be used to estimate the composition of individual pulp samples for a certain cooking time in the studied interval, and it is also a way to summarize experimental data. See the Experimental section for more details concerning the determination and calculation of the composition of wood and pulp samples.

Table 4. Experimental Results Summarized using the Equation ln $W_i = a \times t + b$

Lab Acid Cooking Liquor				
	a	***b***	**R²**	***W*ᵢ (*t*=0)**
Yield	0.2	4.5	0.98	90
Lignin	0.1	3.1	0.92	22.2
Glucomannan	0.28	2.5	0.92	12.2
Xylan	0.3	1.7	0.92	5.5

Notes: "W_i" is the content of the studied component, *"i," "a,"* and *"b"* are constants, and "*t*" is the cooking time. The weight of initial wood chips was defined as 1.0, and "Wi" in the table is given for zero cooking time, *i.e.*, when the cooking temperature was reached.

The pH profiles of the cooking liquor with either mill-prepared or lab-prepared cooking acid are shown in Fig. 5. It is clear that the stability of the pH of the cook using the mill-prepared acid cook was higher than the corresponding pH using the lab-prepared acid. The presence of dissolved organic and inorganic chemical components seemed to act as a buffering agent. The mill acid had a COD content of 49 g/L, which was due to the presence of dissolved organic and inorganic components from the mill.

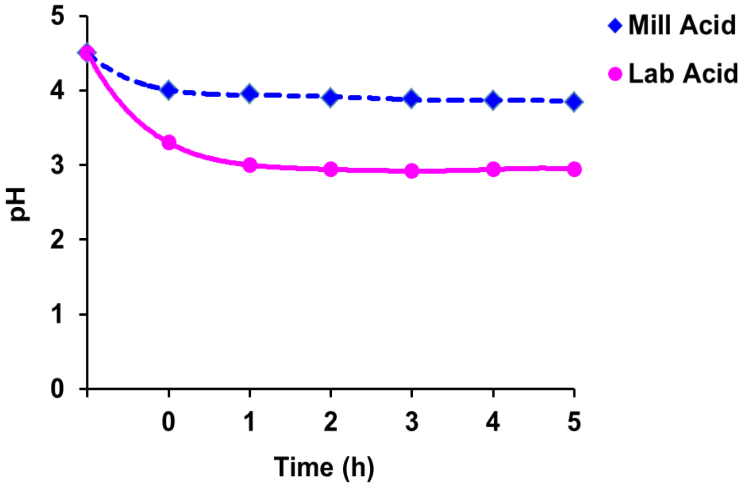

Fig. 5. The pH of the bisulfite liquor phase of the cooking experiment when using mill- or lab-prepared cooking acid. The initial compositions of the cooking acids were the same as in Fig. 2.

During bisulfite cooking, there are also some organic acids generated, such as acetic acid, formic acid, uronic acid, and aldonic acid, and these tend to decrease the pH and the stability of the cooking acid (Husband 1957). The initial pH values of the lab-prepared and mill-prepared bisulfite cooking acids were both 4.5, and the initial chemical concentration with respect to total SO_2 and combined SO_2 were the same in both cases.

The extractives content in the pulp samples, using acetone as the extraction liquor, is shown in Fig. 6. The extractives content in the pulp was higher for the lab acid cook compared with the mill acid cook. The higher extractives removal for the mill acid could be due to the higher pH throughout the cook, as shown in Fig. 5. The higher pH in the mill acid cooking experiments was probably due to the presence of dissolved organic and inorganic components, which act as buffering agents. After 5 h of cooking time, the mill acid liquor phase had a final pH of 3.9, and the lab acid cook had a final pH of 2.9. The acidity in the lab prepared cooking acid increased with cooking time, and the decrease in pH probably hindered the dissolution of extractives into the cooking liquor. Earlier studies by Mutton (1962) showed that acidic pH levels have little hydrolytic effect on the extractives. The shift in the pH during the course of cooking, coupled with the presence of dissolved organic and inorganic components, probably had an impact on the extractives content dissolution into the cooking liquor.

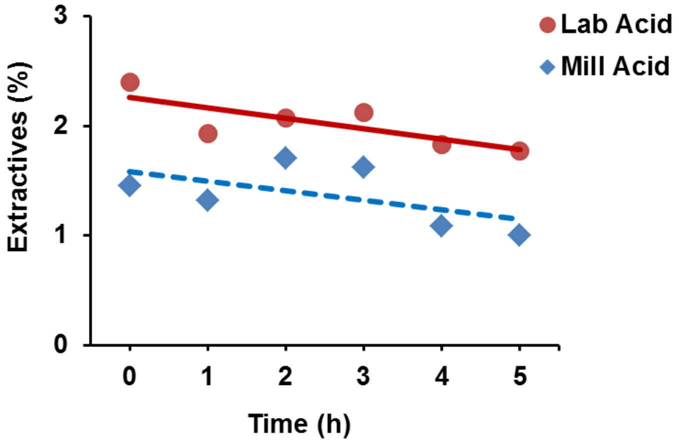

Fig. 6. Acetone extractives content in the pulp after bisulfite cooking of pine with either mill-prepared or lab-prepared cooking acid. The conditions used were the same as in Fig. 2.

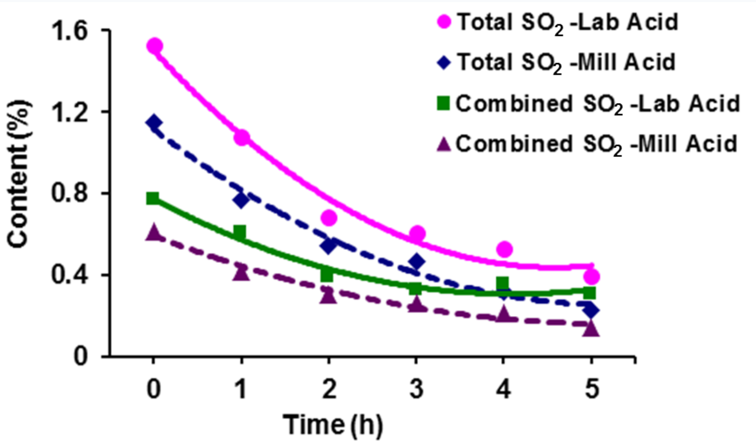

Fig. 7. The content of cooking chemicals in a bisulfite cook, with respect to total and combined SO_2, for the mill- and lab-prepared acids. Conditions used were the same as in Fig. 2.

The contents of total and combined SO_2 during the cook are shown in Fig. 7. It can be seen that the rate of consumption of the cooking chemicals was higher in the case of the mill acid compared with the lab acid, indicating a faster delignification rate for the mill acid. The combined SO_2 concentration after 5 h of cooking time reached a value of zero, indicating that the cook was extended beyond 5 h, and lignin condensation reactions may have occurred (Kaufmann 1951).

The cellulose, hemicelluloses, and extractive contents *versus* the delignification for bisulfite cooking of pine with lab-prepared acid are shown in Fig. 8. The cellulose content was unaffected, and the unchanged value was probably due to its high crystallinity, which made the cellulose very unreactive. The portion of the wood composed of hemicelluloses was more easily attacked because of its amorphous state and relatively low degree of polymerization (Sjöström 1993).

The xylan content of the hemicelluloses was lower in the original wood compared with the glucomannan content and was subjected to hydrolytic degradation reactions. The glucomannan content was more stable when subjected to acid hydrolysis than xylan; however, there was substantial dissolution of glucomannan during bisulfite cooking, as can be seen in the figure (Meier 1962). Earlier studies by Meier and Annergren have shown that delignification was accompanied by partial hemicellulose removal (Annergren and Rydholm 1959; Meier 1962).

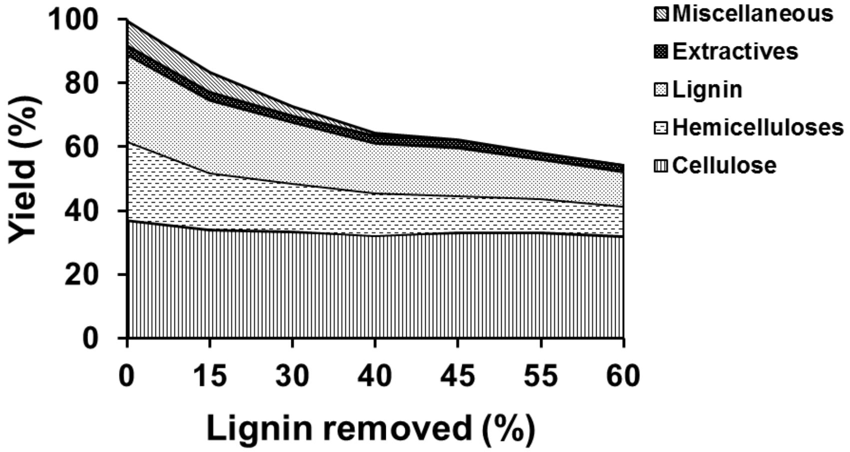

Fig. 8. The carbohydrates and extractives contents *versus* the lignin content for bisulfite cooking of pine using lab-prepared cooking acid. Conditions used were the same as in Fig. 2. The component termed “miscellaneous” in the figure corresponds to the other pulp components and is composed of pectins, proteins, ash, and other polysaccharides.

Figure 9 shows the sulfur-to-lignin (S/L) ratio for spruce and pine during bisulfite cooking, using a mill-prepared cooking acid. The S/L ratio increased with increasing cooking time and was found to reach a maximum value after 3 h. Thus, the S/L ratio was found to level off after 3 h of cooking time, indicating that the dissolution of sulfonated lignin only required 0.06 g of sulfur per gram of lignin. Sulfur content above this level probably caused the lignin to fragment, separate from the fibers, and dissolve in the liquor phase. The S/L ratio showed the same pattern for spruce and pine wood, indicating that there was no difference in the sulfonation rate when pine and spruce were used.

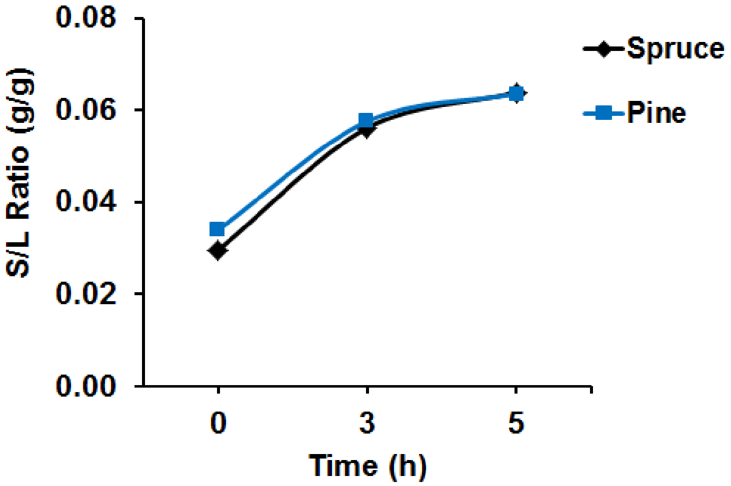

Fig. 9. Sulfur-to-lignin ratio *versus* cooking time for bisulfite cooking of spruce and pine. Conditions used were same as in Fig. 2.

CONCLUSIONS

1. The glucomannan and xylan removal rate was found to be higher for the mill acid cooking experiments, and the cellulose content in both cooking acid cases was unchanged, down to a pulp yield level of approximately 60%.
2. The extractives removal rate was found to be higher in the mill acid experiments, which could be due to a higher pH during the cook when the mill acid was used.
3. The side reactions with respect to thiosulfate formation were found to be higher when lab-prepared acid was used, indicating that the lignin condensation reaction risks were greater when lab-prepared acid was used.
4. The S/L ratio increased with cooking time up to approximately 0.06 g sulfur content per gram of lignin. The value was the same for both spruce and pine wood.
5. The experimental results were used to develop an equation that will allow researchers to obtain the pulp composition with respect to lignin and carbohydrate content.

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