INITIAL PHASE OF SODIUM BISULPHITE PULPING OF SPRUCE.

PART I

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A sodium bisulphite cooking study has been performed on spruce chips with the aim of monitoring the impregnation and the initial phase of such a cook performed at pH 4.5. Both pulp and liquor analyses have been carried out and the experiments have been done with a laboratory-prepared cooking acid, in comparison with a mill cooking acid. The pulping experiments have been performed down to a total pulp yield of 60%. The objective was to verify and extend the current knowledge of bisulphite pulping with a focus on the initial phase of the cook. With the help of a kinetic model that has been developed in the project, the pulp composition during the cook with respect to cellulose, lignin, glucomannan and xylan can now be predicted. The side reactions with respect to thiosulphate formation were also analyzed in this study.

Keywords: bisulphite cooking, cellulose, glucomannan, kinetics, lignin, spruce, thiosulphate and xylan

INTRODUCTION

Before about 1950, two sulphite pulping processes, i.e. acid sulphite and bisulphite, were together the dominating chemical pulping technologies used in pulp mills and thus kraft pulping was less common. One reason to the dominance of the sulphite pulping processes versus kraft pulping was due to the lower investment and operating costs for the small and relatively simple mills used at that time with, in many cases, no chemical recovery system. Other reasons were the high brightness of the pulps after the cook, making bleaching in some cases unnecessary, while kraft pulp always needed bleaching when high pulp brightness was of interest. The higher pulp yield for softwood sulphite pulps was also a reason to choose a sulphite process. However, when chlorine dioxide bleaching was invented in the end of the 1940s, it became possible to produce also kraft pulps with high brightness. Softwood kraft pulps were also stronger than sulphite pulps and their wood raw material requirement was much less demanding. Finally, a kraft pulp mill always has a good chemical recovery system, as the cooking chemicals must be reused due to economic reasons, making the environmental impact from a bleached kraft pulp mill low. All these reasons have made kraft pulping the currently dominating process for chemical pulp production and only a few sulphite pulp mills are still operational on date. One indirect result of this decreasing trend for sulphite pulping was that research and development concerning the sulphite processes decreased and it more or less stopped in the 1980s. However, there are still bleached sulphite mills in operation in Europe and North America and three of these mills are in Sweden. Sweden has also two pulp mills that produce neutral sulphite semi-chemical pulps (NSSC) based on birch, where the pulp is mainly used as unbleached corrugated medium in container board, but this pulp grade is not further discussed in this manuscript.

Important early contributions in the development of the sulphite processes were done by many people, for example, Calhoun,[1] Beazley[2] and Miller.[3] They investigated, for example, variables that could be used to control the delignification rate of a sulphite cook, but also the wood chemistry, as for example the sulfonation reactions of the pulp. Especially important were the contributions of Hägglund,[4] Häggroth[5] and

Rydholm.[6] Many early investigations in sulphite pulping were focused on the hemicellulose content in the pulp and how that content could be kept in the fibers during cooking instead of being dissolved and lost in the filtrates. Annergren,[7,8,9] Schöön,[10,11] Rydholm[12] and Sixta[13] have done great studies in this research area. This knowledge could naturally also be used to increase the degree of dissolution of hemicellulose from the pulp during cooking, which is important for dissolving pulps.

However, it is well-known that during a sulphite cook, there are beneficial reactions that mainly delignify the pulp, but also several undesirable ones, which decompose the cooking liquors or react with the cellulose and/or the hemicellulose.[8,9,12] The formation of thiosulphate and sulfate during sulphite pulping can, for example, be used as an indicator of the extent of unwanted reactions. If the pulping conditions in a given sulphite stage also lead to a low content of cooking chemicals, and especially a low content of "combined SO_2", there is a high risk for lignin condensation reactions at the end of the cook, which in the worst case, can lead to a so-called black cook, where the pulp is totally black and useless.[14]

Detailed studies on the cooking chemistry and especially the formation of thiosulphate and sulfate during the cook were done in the 1960s by Sjöström and Schöön.[10,11,15] Although all these studies were good, they are about 50 years old and it is therefore necessary that an updating of the old knowledge be done. The objective of this first study (Part I) was to verify old results concerning single-stage bisulphite cooking of spruce, and to establish a reference case for the subsequent multi-stage bisulphite cooking experiments when lab-prepared and mill-prepared cooking acids were used.

EXPERIMENTAL

Spruce (*Picea abies*)chips were collected from a Swedish pulp mill, 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 retained on the 13 mm tray were used for the experimental trials("Ø" represents slots 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 needed for the cooking experiments.

Mill-prepared bisulphite cooking acid was needed for some of the reference experiments and its composition is given in Table 1. However, in the majority of the experiments, a lab-prepared bisulphate cooking acid was used and its composition is also given in Table 1. The starting pH of the cooking liquor used for the bisulphite cooking experiments was 4.5 measured at room temperature.

The cooking experiments were carried out in 6 autoclaves of 1 litre each and these autoclaves were slowly rotating in a glycol bath, in which they were heated according to a predetermined temperature profile, as illustrated in Figure 1. The startup temperature was 100 °C and the L/W-ratio was always 4.6. The temperature was raised 1 °C/min up to an intermediate temperature, where time was given for the final impregnation of the chips, after which the temperature was raised again during 1 h up to the final cooking temperature. Note that the time 'zero hour' was defined as the time when full cooking temperature was reached, which means that the time when the autoclaves were mounted into the digester was negative, in this case minus 2 h, as shown in Figure 1.

The initial amount of chips in each autoclave was 100 g, calculated as oven-dry material. The cooking acid always had a total SO_2 content of 2.7%, a combined SO_2 of 1.5% and a free SO_2 of 1.2% calculated as SO_2. The base (cation) charge was 5% measured as Na_2O and calculated with wood as the reference. Sulphite cooking liquors are usually analysed for total SO_2, free SO_2 and combined SO_2, determined by an iodometric titration, followed by further titration with NaOH. The total SO_2 summarises 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 cations ("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 thus, approximately, the difference between the total $SO_2$and the combined SO_2.

At the end of each cook, the autoclaves were cooled rapidly by submerging them into cold water of about 10 °C to stop further reactions. Pulp and liquor samples were then collected. The pulp samples obtained were washed overnight with distilled water and then dried at 45 °C in an oven to air-dried equilibrium conditions. After drying, the different cooked chip samples were ground in a Wiley Mill to get a wood powder that passed slots of 0.4 mm (40 mesh), and these powder samples were finally used for analysis of the different components, as mentioned in Table 2.

The spent cooking liquors were analyzed as described in Table 3. The composition of the pulp with respect to lignin, extractives, cellulose, glucomannan and xylan was based on Klason and UV lignin determination of the acetone-extracted chips.

Table 1
Composition of the two cooking acids used in the experiments prior to the addition of SO_2

	Mill prepared cooking acid	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
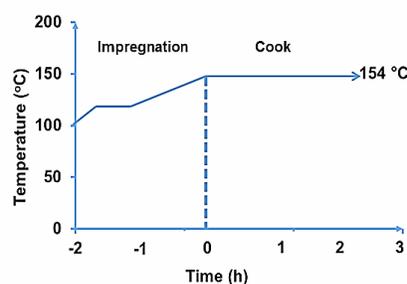
Figure 1: Temperature profile during the laboratory cooks; cooking temperature: 154 °C;
L/W-ratio was always 4.6

Table 2
Testing methods used for the wood and pulp samples

Acetone extract	ISO 14453
Klason lignin	Tappi T-UM 250
Lignin (UV)	Tappi T 222
Arabinose, galactose, glucose, mannose and xylose	SCAN-CM 71:09[*]
Total-S	SCAN-CM 57

[*]Calculated as anhydrous sugar

Table 3
Testing methods used for spent liquors

Sulfate	SCAN-N 36
Lignin	Tappi T-UM 250
Acetone extract	KA 11.305
Sulphite	SCAN-N 36
Arabinose tot., galactose tot., glucose tot., mannose tot.and xylose tot.	KA 10.202
Thiosulphate	SCAN-N 36
Total-S	SCAN-N 35

The carbohydrate analysis was carried out using IC (Ion Chromatography) and the calibration was done using external standards. The carbohydrate monomer values obtained were recalculated to the initial carbohydrate polymers by using the correlations of Meier.[16] However, while analyzing the carbohydrates

in this way, there is always a significant fraction of the pulp that is impossible to dissolve and it is therefore reported as a "residual". This is at least 10%, but in some cases 20-30%, of the bone dry pulp weight. Some laboratories do not report this amount at all, due to the fact that this amount does not respond to the

carbohydrate test and it is therefore considered to be "something else", although it is well known that wood and pulp consist 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 monomer. This water is bound to the monomers in its monomer state, but not bound to the monomers in the polymeric state. Thus, published carbohydrate numbers for wood and pulp samples have to be checked very carefully to avoid erroneous conclusions. The bound water has, in this study, been subtracted and we have not included the residual in the carbohydrate numbers, which means that our numbers for cellulose, glucomannan and xylan are on the low side, compared to old numbers reported in different textbooks, for example that by Rydholm.[12]

The methoxyl groups in the wood and pulp was determined basically by cleaving them with hydroiodic acid (and adipic acid as a catalyst), giving methyl iodide, which is analyzed with GC (Gas Chromatography).

The final pulp sample evaluation was done according to the correlation "Ln Wi = a x t + b", where "Ln Wi" is the logarithm of the parameter "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 the second constant and "t" is the cooking time. Due to the non-constant cooking chemical concentrations during the pulping reactions, the kinetic data evaluation had to be based mainly on the initial chemical concentrations.

RESULTS AND DISCUSSION

A spruce bisulphite cook was carried out, where two types of cooking acids were used (see "EXPERIMENTAL" section). The residual liquor composition during the cook is shown in Figure 2.
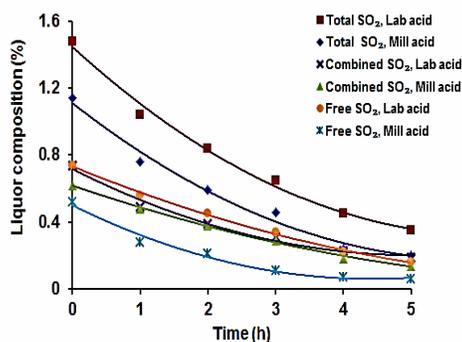
As indicated in Table 1, the initial concentration of cooking chemicals was the same in both cases.

Figure 2 reveals that the concentration of cooking chemicals was the lowest for the experiments in which mill-prepared cooking acid were used, thus, the content of COD and inorganic ions in the mill cooking liquor case seemed to catalyze the chemical reactions during the cook. The practical conclusion of this result is that studies of sulphite pulping should be done using lab-prepared cooking acids as decomposition reactions then seem to be small or at least smaller than if mill cooking acids are used. Secondly, the correlations shown for free, combined and total SO_2 are slightly curved and they begin to level out at the end of the cook. It can also be seen that the content of combined SO_2 tends to reach the zero level after a cooking time of about 5 h. Thus, if the experiments had been prolonged for one more hour, extensive lignin condensation reactions would most probably have started up, and the risk for a so-called black cook would then have been high, according to Kaufmann.[14]

As is usually the case in chemical pulping reactions, these can, in most cases, be approximated as first order reactions.[17,18,19,20,21] This is also the case in this study, as shown for the total SO_2 concentration and its logarithmic value in Figure 3. Thus, the linear logarithmic correlation shown in the figure verifies that the studied reaction can be assumed to follow a first order reaction with respect to the total SO_2 concentration.
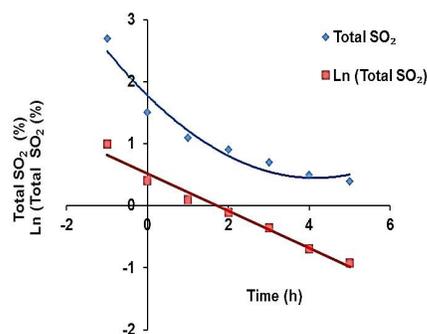

Figure 2: Total SO_2, combined SO_2 and free SO_2 levels in laboratory experiments where either mill-prepared or lab-prepared cooking acid was used. The initial composition of the cooking acids was always: Total SO_2 2.7%, combined SO_2 1.5% and free SO_2 1.2%, calculated as SO_2; L/W-ratio 4.6; base content 5%, calculated on the weight of dry wood chips and as Na_2O; temperature 154 °C

Figure 3: Total SO_2 and the logarithmic value of the total SO_2 for the cooking experiment shown in Figure 2. As the logarithmic correlation is linear, the chemical reaction can be assumed to be of first order with respect to total SO_2
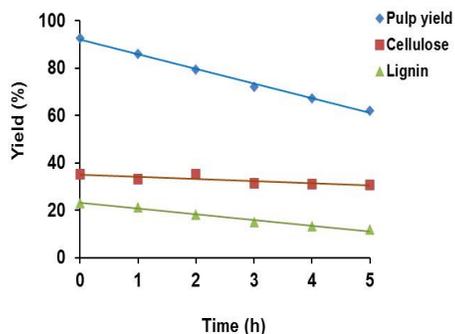
Figure 4: Bisulphite cooking of spruce with a laboratory-prepared cooking acid. Conditions used: total SO_2 2.7%, combined SO_2 1.5% and free SO_2 1.2%, calculated as SO_2; base charge 5%, calculated as Na_2O and on dry chips; temperature 154 °C. Note that time zero was defined as the time when full cooking temperature was reached, which means that the time when the autoclaves were mounted into the digester was "minus 2 h"
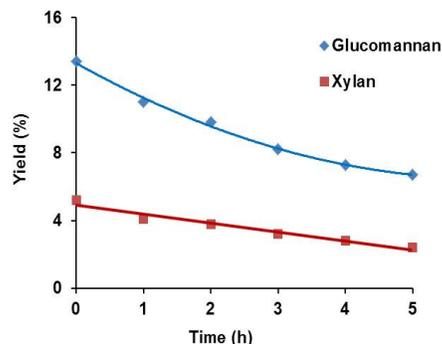

Figure 5: Glucomannan and xylan contents in the pulp during bisulphite cooking of spruce with lab-prepared cooking acid. The temperature was 154 °C. Time zero was defined as the time when full cooking temperature was reached and the time when the autoclaves were mounted into the digester was "minus 2 h"

The "pulp yield", the "cellulose yield" and the "lignin yield" were analyzed and the results for the cooking experiments with the lab cooking acid are shown versus cooking time in Figure 4. The yield of the different components can be seen as being low, compared to commonly used numbers in old textbooks, but this can be explained as being due to both the yield loss prior to the attainment of the full cooking temperature, i.e. up to "time zero", and to the exclusion of bound water and non-cellulosic material, as described in the "EXPERIMENTAL" part.

It can be noted that the correlations in the figure are surprisingly straight even though this cook was prolonged down to a pulp yield of approximately 60%. The cellulosic yield was not affected at full cooking temperature, which can be attributed to its high degree of crystallinity.[12,13] The unaffected cellulose yield was interesting as in old textbooks, it is claimed that the yield in a sulphite cook is totally unchanged down to about 50% total pulp yield. The experiments carried out by the authors revealed that this was true up to approximately 60% total pulp yield.[12,15] To conclude, it can be claimed that the pulp yield and the lignin yield decreased with increasing cooking time, and the rate was higher for the losses of the pulp and lignin yields vis-à-vis that of the cellulose yield.

The corresponding results for glucomannan and xylan in the pulp samples are shown in Figure 5. It can be seen that these correlations were also very linear, although the cooking time at full

cooking temperature was as long as 5 h. The steeper slope of the glucomannan yield, with respect to the xylan yield means that the glucomannan content decreased faster and the contents of the two hemicellulose components in the pulp therefore evened out with increasing cooking time.

The correlations for cellulose, lignin, glucomannan and xylan in the pulp using a lab-prepared cooking acid have been summarized in Table 4 using the general equation "Ln Wi = a x t + b", where "Wi" is the actual parameter, "a" and "b" are constants, and "t" is the cooking time (see "EXPERIMENTAL"). Note that time zero hour was defined as the time when full cooking temperature was reached, which means that the time when the autoclaves were mounted into the digester was negative, in this case minus 2 h. The equations 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 the experimental data. See also "EXPERIMENTAL"section for more details concerning the composition of wood and pulp samples.

The experimental results for cooking with lab acid are summarized in the equation "Ln Wi = at+b", where "Wi" is the content of the actual component "i", "a" and "b" are constants, and "t" is the cooking time (Table 4). The weight of the initial wood chips was defined as 1.0 and "Wi" in Table 4 is given for zero hour cooking time, i.e. when the final cooking temperature was reached.

It is well known that the chemical reactions in a sulphite cook lead to the formation of sulphonic groups ($-SO_3H$) in the lignin, and that these groups facilitate the degradation and the subsequent dissolution of the lignin from the pulp.[12] The amount of sulphonic groups in the pulp is thus an important parameter, and it can be approximately analyzed as the ratio of the total amount of sulfur in the pulp to the total amount of methoxyl groups in the same pulp. Rydholm[6] reported that this ratio levels off at 0.3 mol S/mol OCH_3 in the wood residue, thus this level seems to be sufficient for good delignification. Figure 6 graphically depicts one of the results of the experiments. Thus, the figure shows that for this cook, the maximum ratio was obtained after 3 h and the ratio was then about 0.3 mol S/mol OCH_3. It can also be seen that the mol S/mol OCH_3 ratio and the delignification ratio correlated up to a cooking time of 3 h. For longer cooking times, the degree of delignification increased further, while the mol S/mol OCH_3 levelled out and then decreased. One can conclude that the content of

sulphonic groups in the pulp is particularly important in the initial part of the cook.

The formation of thiosulphate, which is a degradation product from the charged cooking chemicals, is one variable that can be used to monitor the efficiency of the cooking reaction. Especially in the initial phase of a sulphite cook, before the lignin is properly sulfonated, it is a risk that the generated thiosulphate will react with the lignin and thus result in lignin condensation reactions.[22] The thiosulphate content should not therefore be too high in a pulp mill; it should not be above 1.7 g/l (0.015 mol/l), according to Rydholm.[12] It has been found that immediately before a so-called black cook is obtained, the thiosulphate concentration in the liquor phase can be as high as 3 g/l (0.026 mol/l).[12] However, as the thiosulphate is consumed in the lignin condensation reactions, its concentration decreases rapidly when the black cook reactions start up. The results obtained in our experiments are far below the critical thiosulphate level, as seen in Figure 7.

Table 4
Experimental results for cooking with mill acid

Components	a	b	Wi (t=0)	R^2
Cellulose	0.13	3.54	34.5	0.92
Lignin	0.38	3.2	24.5	0.91
Glucomannan	0.4	2.6	13.5	0.97
Xylan	0.4	1.7	5.5	0.94

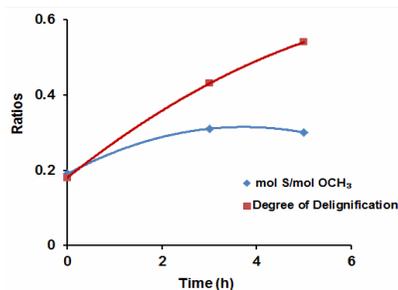
Figure 6: Degree of sulfonation measured as mol S/mol OCH_3 and the degree of delignification during bisulphite cooking of spruce (temperature 154 °C)
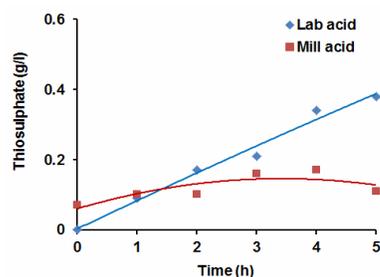
Figure 7: Thiosulphate content in the cooking liquor during bisulphite cooking of spruce with lab-prepared or mill-prepared cooking acids. The lower thiosulphate number for the mill-prepared acid experiments was probably due to more lignin condensation reactions, which reduced the thiosulphate content in the free liquor phase
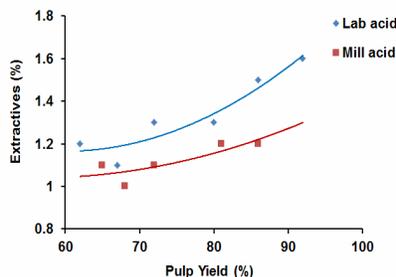
Figure 8: Acetone extractives content in the pulp during bisulphite cooking of spruce with a lab-prepared and a mill prepared cooking acid

It is also indicated in Figure 7 that the thiosulphate content increased more in the lab acid experiments vis-à-vis the mill acid ones. After 5 h, the difference between the two cases was conspicuous; about four times higher in the former. It should be noted at this juncture that the initial mill acid had a thiosulphate content of 0.8 g/l, while the thiosulphate concentration in the spent cooking liquor was always below 0.2 g/l, indicating that thiosulphate lignin condensation reactions had taken place. As mentioned earlier, the initial pH was the same in both cases (4.5), but in the experiments using the lab-prepared cooking acid, the pH decreased more than in those in which the mill cooking acid was used, probably due to a lower buffering capacity in the former. Thus, it seems that bisulphite pulping with a lab-prepared cooking acid cannot be used to forecast the thiosulphate concentration that will be obtained in a bisulphite cook in a pulp mill.

The lower the extractives content in the pulp after the cook the better. As extractives have a poor solubility in water, especially at lower pH values. Extractives can therefore cause scaling and clogging of process equipment in a pulp mill, which can be very disturbing for the pulp mill. The analysis of the extractives content is done by pulp extraction with a liquid of low polarity, for example, alcohol, ether or acetone. In this study, acetone has been used. Finally, a gravimetric determination of the solubilized material was done.

The content of extractives in the pulp is shown in Figure 8 for mill-prepared and lab-prepared cooking acids. As seen, the extractives content is higher in the latter case. The reason for the difference could be the lower content of ions and organic matter in the lab-prepared cooking acid, which should facilitate dissolution of the extractives. Secondly, there was a difference in the final pH between the two cooking experiments although the initial pH was the same, i.e. 2.9 for

the lab-prepared acid cook vs 3.8 for the mill-prepared acid cook. A lower pH should theoretically be detrimental to the dissolution of extractives during pulping. Thus, to be able to predict the final extractives content in the pulp in a pulp mill by performing laboratory experiments, it is important to use a cooking acid composition that is equal to that of a mill-prepared cooking acid.

CONCLUSION

In the initial part of a spruce bisulphite cook, it was found that the cellulose yield was unchanged down to a total pulp yield of about 60%. However, in old textbooks, it is claimed that the cellulose yield is unchanged down to as low a pulp yield as 50%. It was possible to summarize the lignin and carbohydrate dissolution rates using the equation "Ln Wi = a x t + b", where "Wi" is the studied variable, "a" and "b" are constants, and "t" is the cooking time. The equation can be used to predict the pulp composition during the cook vs the cooking time. The study also showed that the thiosulphate content in the liquor phase and the extractives content in the pulp were much lower if a mill-prepared cooking acid was used instead of a lab-prepared one. Thus, to be able to simulate the situation in a pulp mill by performing laboratory experiments, it is important to use the correct composition of cooking liquor.

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