

THE INFLUENCE OF THE TEMPERATURE ON THE INITIAL PHASE OF SODIUM BISULFITE PULPING OF SPRUCE

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ABSTRACT

The initial phase of a bisulfite cook, here defined as the first part of the cook down to 20% lignin, is highly influenced by the temperature and it can therefore be used to control the initial pulping rate with respect to lignin. However, the influence of the temperature is different for the degradation of lignin, hemicellulose and cellulose and for the formation of the by-product thiosulfate. The temperature is therefore a powerful tool to control several mechanisms in a bisulfite cook.

Additionally, if the cooking acid is taken from a pulp mill, where the ionic strength, the content of by-products and COD in the liquor phase are much higher than in a lab prepared cooking acid, this will also influence the kinetics of the different chemical reactions and, thus, the composition of the pulp after a certain cooking time. Earlier literature references, which are based on lab prepared cooking acids, are therefore not completely reliable as tools to predict the final composition of the pulp in a pulp mill.

Keywords: Bisulfite pulping, cellulose, glucomannan, kinetics, lignin, spruce, thiosulfate and xylan.

INTRODUCTION

Sulfite pulping of any type is today practiced in only a small number of pulp mills around the globe, and the number of these sulfite pulp mills that use sodium as the base (cation) is probably between one or two. However, due to the increasing interest in the wood based biorefinery concept, the benefits of sulfite pulping, and especially the sodium based variety, has recently started to gain a lot of interest. One reason to this latter trend is probably the commercial success of the Domsjö Fabriker dissolving pulp mill in Örnsköldsvik, Sweden [1]. It was therefore of interest to further study the sodium based sulfite process to investigate if its benefits could be even better utilized in the future in the production of dissolving pulps. Of specific interest was to investigate if a multiple stage sulfite process could be beneficial and, furthermore, to find the most effective pulping conditions in the initial part of

the cook, here defined as the first part of the cook down to 20% lignin, **Figure 1**. As sulfite pulping historically has been studied in detail by several researchers, their results have been a good starting point for our project. Thus, our study is based on the classic studies of Annergren *et al.* [3,4,5], Kaufmann [6], Rydholm [7,8], Schön *et al.* [9,10], Sixta [11] and Sjöström *et al.* [12].

EXPERIMENTAL

Spruce chips from the Domsjö pulp mill 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 retained on the 13 mm tray were used for the experimental trials. Knots and chips with bark were manually removed. The acceptable chips were frozen and stored until needed for the cooking experiments.

Mill prepared bisulfite 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 bisulfite cooking

Table 1. The composition of the two cooking acids used in the experiments analyzed directly after the addition of the cooking chemicals

	The mill prepared cooking acid	The lab prepared cooking acid
COD g/L	52	0
Total SO ₂ , %	2.7	2.7
Free SO ₂ , %	1.2	1.2
Combined SO ₂ , %	1.5	1.5
Na ₂ S ₂ O ₃ , g/L	1	0
Na ₂ SO ₄ , g/L	3	0
pH	4.5	4.5

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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 always 4.5, measured at room temperature.

The cooking experiments were carried out in 6 autoclaves of 1 liter each, and these autoclaves were slowly rotating in a glycol bath where they were heated according to a predetermined temperature profile. 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 1h up to the final cooking temperature. 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 thus defined as "minus 2 hours".

The initial amount of chips in each autoclave was 100g, calculated as oven dry material. The cooking acid had a constant total SO₂ content of 2.7% and a combined SO₂ of 1.5% at the start of cook. The base (cation) charge was 5% measured as Na₂O on wood. 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, pulp samples were ground in a Wiley Mill to 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 acetone extracted chips. The carbohydrate monomer values obtained were recalculated to the initial compounds by using the correlations of Meier [13]. However, when analyzing the carbohydrates in this way there is always a significant fraction of the pulp that is not possible to dissolve and it is therefore reported as a "residual", which is at least 10%, but in some cases 20%-30% of the initial 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". 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

Table 2. Testing methods used for the wood and pulp samples

Klason lignin	Tappi T-UM 250
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
Arabinose Tot., Galactose Tot., Glucose Tot., Mannose Tot. and Xylose Tot.	KA 10.202
Thiosulfate	SCAN-N 36

monomer in its monomer state, but not bound to the monomers in the polymer 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 amount", which means that our numbers for cellulose, glucomannan and xylan are low compared to old numbers reported by, for example, Rydholm [7].

RESULTS AND DISCUSSION

This study on bisulfite cooking of spruce was focused on the initial stage of the bisulfite cook and referred to as Phase-I in the **Figure 1**, here defined as the part of the cook down to 20% lignin. The rest of the cook was defined as Phase-II.

Sulfite pulping is a chemical process that is used to degrade the lignin in the wood chips and it will, thus, lead to a separation of the wood fibers prior to a subsequent formation of either a fiber network in a paper matrix or a first stage in the preparation of cellulose chemicals or regenerated cellulose. Thus, in the cook, the most important reactions are the ones between the lignin in the wood and the cooking acid, and these reactions are highly influenced by the temperature, **Figure 2**.

If using the Arrhenius equation to describe the influence of the temperature on the initial pulping rate, the activation energy was found to be 130±5 kJ/mole, **Table 4**. This value corresponds to an increase in the cooking rate by 2.5-3 times for an increase in the temperature of 10 °C. The corresponding numbers found

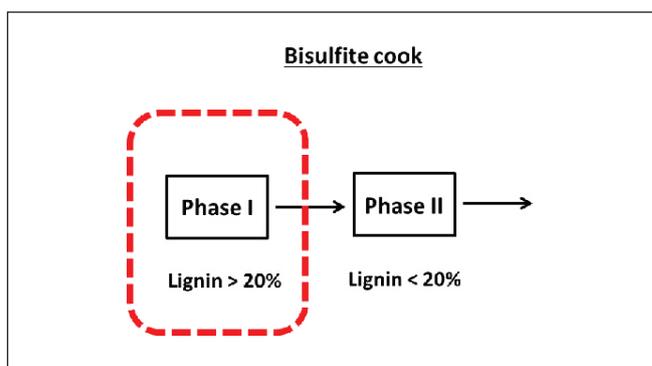


Figure 1. The bisulfite cook was divided into an initial phase (phase I where lignin content was above 20%) and a second phase (phase II) that included the rest of the cook

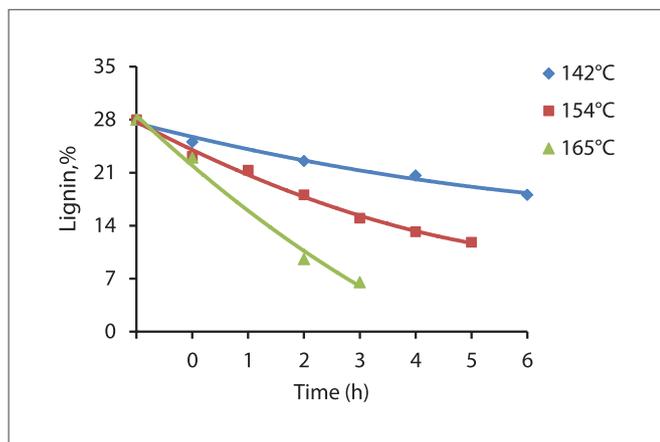


Figure 2. Influence of time and temperature on the lignin degradation during bisulfite cooking of spruce. Conditions used: 2.7% total SO₂ and 1.5% combined SO₂. The cooking acid was prepared in the lab

by other researchers for the combined initial and final part of bisulfite pulping are 80-90 kJ/mole [14, 15, 16].

Compared with the delignification reactions, which are highly influenced by the temperature, the cellulose is not reactive in the beginning of the cook, and is therefore not influenced by an increase in temperature, **Figure 3**. This behavior of the cellulose depends on the high crystallinity of the cellulose, which makes it hard for the cooking acid chemicals to penetrate the cellulose matrix [3,5,7,8]. Thus, the figure shows that even if the lignin content was reduced by as much as 50%, the cellulose content was more or less unchanged. As the influence of the temperature is zero, so is the activation energy for the cellulose in the initial phase of the cook, **Table 4**. This low reactivity is specific for sulfite pulping and quite different compared with kraft pulping, where the cellulose is slowly degraded already from the start of the cook [17]. Note in the figure that the y-axis is not crossing the x-axis at origo, but rather about one hour earlier. The reason is that the lignin reactions start already in the impregnation phase, although the full reaction temperature is not reached until the time is "zero" hours.

The hemicelluloses, i.e. glucomannan and xylan, are not crystalline like the cellulose and the hemicellulose molecules are relatively short [18]. Thus, these molecules are affected by the cooking acid and they are, therefore, degraded from the start of the impregnation phase of the cook. It is clear that in a bisulfite cook the hemicellulose content will be reduced by more than 50% in the

Table 4. The activation energies found in this investigation for the different wood components, in here defined as the initial reaction down to 20% lignin for a bisulfite cook using spruce

Wood component	E _a , kJ/mole
Lignin	130±5
Cellulose	0
Hemicellulose	87±4

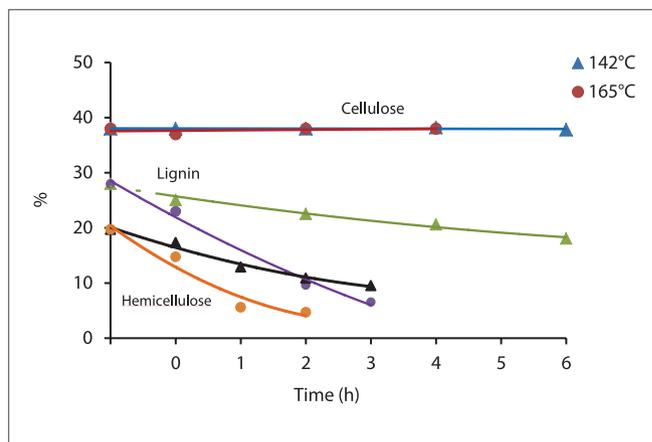


Figure 3. Influence of time and temperature on the cellulose degradation and as a reference the lignin and hemicellulose degradation during bisulfite cooking of spruce. Conditions used: 2.7% total SO₂ and 1.5% combined SO₂. The L/W-ratio was 4.6. The cooking acid was prepared in the lab

initial part of the cook, here defined as the first part of the cook down to 20% lignin, **Figure 3**. The activation energy found for the hemicellulose degradation was, in our study, 87±4 kJ/mole, thus lower than for the lignin reaction. The hemicellulose results are in good agreement with earlier results by Goldfinger and Kaufmann, who have reported activation energies between 71-88 kJ/mole [6,14]. However, the activation energy for hemicellulose degradation is much higher than for cellulose, **Table 4**. Thus, by changing the temperature it is possible to manipulate the composition of the pulp with respect to lignin and carbohydrates after the digester. For example, if a low hemicellulose content and high cellulose content are demanded in the final pulp, the temperature should be as high as possible and vice versa. Dissolving pulp is an example of the first type and greaseproof pulp an example of the second.

It is obvious that the pulping reactions during cooking decrease the lignin content in the wood, and these reactions naturally reduces the remaining content of cooking acid, **Figure 4**.

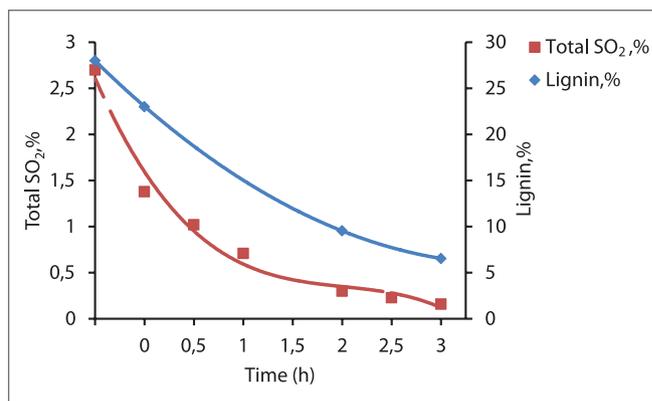


Figure 4. The delignification reaction and the consumption of cooking acid, here given as total SO₂, are highly correlated, as can be seen in the figure. Conditions used were: 2.7% total SO₂, 1.5% combined SO₂, 165 °C and the initial pH was 4.5. The L/W ratio was 4.6. The sodium base charge was 5% calculated as Na₂O on wood

The cooking acid content is here given as the concentration of total SO_2 and it is clear that these two reactions are relatively well correlated, although the initial consumption of cooking acids is higher than the initial lignin degradation. The relatively high initial consumption of SO_2 is due to impregnation and to the fast initial reaction with the lignin. The results in Figure 4 were obtained at 165 °C.

Sulfite pulping is relatively complicated compared to the other commercial cooking processes, for example, kraft cooking. In a sulfite cook there are several different chemical reactions going on at the same time, i.e. degradation of the lignin, degradation of the carbohydrates and then, especially, degradation of the hemicelluloses and finally degradation of the cooking liquor and formation of by-products such as thiosulfate and sulfate. It can therefore be of interest to analyze the content of these two by-products in the liquor phase as a way to determine if the cooking reactions are efficient.

In this study we have seen an influence of the temperature on the formation of the thiosulfate, with thiosulfate formation being higher at higher temperature, **Figure 5**. It is also seen in the figure that if the temperature was very high and the cooking time relatively long there seemed to be a further reaction going on in the liquid phase, which decreased the thiosulfate content after reaching an optimum value. It is generally believed that this reduction in the thiosulfate content is due to a reaction between the thiosulfate and the lignin. This lignin condensation reaction is the first step towards a general lignin condensation reaction, which in the end can lead to the formation of a black cook [6]. Finally, it is also seen that if a mill cooking acid is used, instead of a much purer lab made cooking acid, this has an influence on the thiosulfate level in the cooking acid. This phenomenon is suggested by the authors to be due to a parallel lignin condensation reaction between the dissolved lignin in the liquor phase and the dissolved thiosulfate

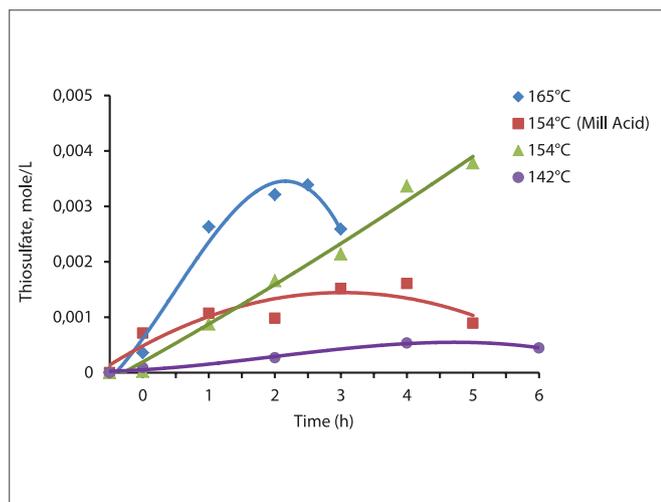


Figure 5. Thiosulfate content in the cooking liquor during bisulfite cooking of spruce with lab and mill made cooking acids at temperature of 142 °C, 154 °C and 165 °C. The mill acid was only used at 154 °C

molecules in the liquor phase. Thus, it can be concluded that a lignin condensation reaction in the liquor phase is not as critical as a corresponding lignin condensation reaction in the lignin that still is bound in the pulp. One conclusion from this figure is that it is not recommended to use a lab made cooking acid if the chemical reactions in the liquid phase, during an industrial cook, are going to be studied, as the conclusions drawn from such an experiment may be very misleading.

In Figure 5 it is also shown that the thiosulfate content in the liquor phase was influenced by the quality of the cooking acid. However, when the reaction rate for the degradation of the lignin in the pulp was analyzed, there was only a small negative influence of using a mill made cooking acid *versus* using a lab made cooking acid, **Figure 6**. The delignification reaction was thus relatively robust and not influenced by the presence of by-products and COD from the mill cooking acid. In fact, the dissolved lignin and other by-products in the liquor phase can have a protective effect on the cook as the lignin condensation reactions, due to the thiosulfate ions, take place to a large extent in the dissolved lignin and not in the lignin that still is bound to the fibers. The slightly lower lignin degradation rate when a mill cooking acid was used can most probably be explained as being due to the higher decomposition rate of the mill liquor, resulting in lower concentration of SO_2 in the liquid phase, **Figure 7**. Thus, the different ions, by-products and COD in the mill cooking acid consumed a certain amount of the charged SO_2 and this additional reaction seemed to take place early in the cook, as shown in the Figure 7. To compensate for the additional consumption of SO_2 , in this case an additional charge of 0.3% SO_2 had probably been needed according to Figure 7.

In bisulfite cooking experiments, done with either a mill or a lab prepared cooking acid, the cellulose content with time remains almost constant in the initial phase of cook due to high crystallinity of cellulose, Figure 2. It is seen that a slightly lower

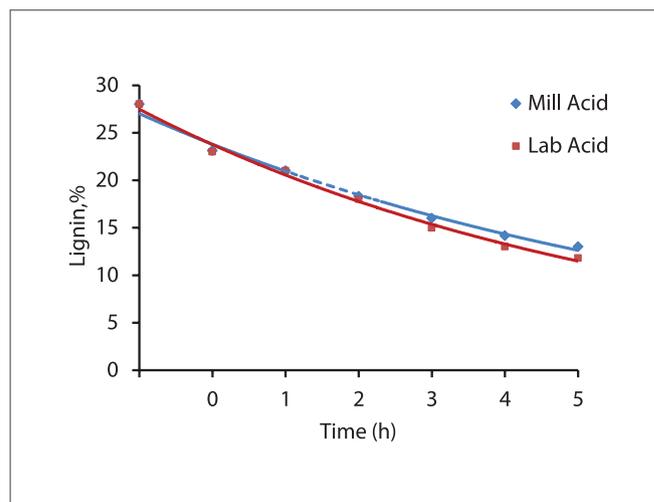


Figure 6. The delignification rate in a bisulfite cook is slightly different if a mill cooking acid is used *versus* a lab cooking acid. Conditions used: 2.7% total SO_2 , 1.5% combined SO_2 , 154 °C and initial pH 4.5

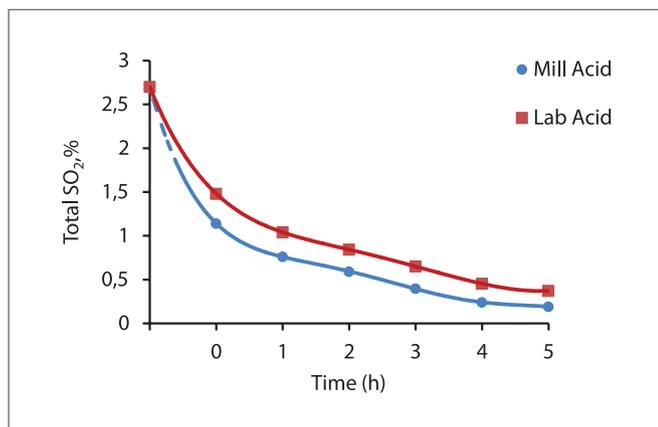


Figure 7. The consumption of cooking acid *versus* cooking time was slightly influenced by the type of cooking acid used

cellulose yield is obtained at prolonged cooking time when using a mill cooking acid, indicating that the reaction rate in the mill acid system is slightly higher than in a lab acid system. Thus, from a cellulose yield perspective it is beneficial to use a lab prepared cooking acid, but it has to be remembered that a lab experiment using a lab cooking acid cannot be used to exactly predict the result of a bisulfite cook in a pulp mill. The same conclusion can be drawn for the degradation of the hemicellulose content, here shown as the hemicellulose content *versus* time, **Figure 8**.

FINAL REMARKS

It has been shown that in a bisulfite cook the rate of delignification, the rate of degradation of the cellulose and of the hemicellulose and, finally, the rate of degradation of the cooking acid are all influenced by the temperature, but to different degrees. It can, for example, be concluded that at a higher temperature a lower content of hemicellulose compared at given cellulose content will be obtained. It can also be concluded that a higher temperature increases the rate of thiosulfate formation and, thus, the risk for lignin condensation reactions and the likelihood for a so-called black cook is therefore higher. Thus, for a bisulfite pulp mill that produces paper pulp and where a high pulp yield is needed, a low temperature is recommended, although this will also increase the total cooking time.

The quality of the cooking acid was shown to be an additional

Table 5. The relative kinetic effect of the mill acid *versus* lab acid for bisulfite pulping of spruce at 154 °C

Reference	Lab acid	Mill acid
Temperature, °C	154	154
Cellulose	0	0
Hemicellulose	0	Higher
Lignin	0	Lower
Thiosulfate	0	Lower

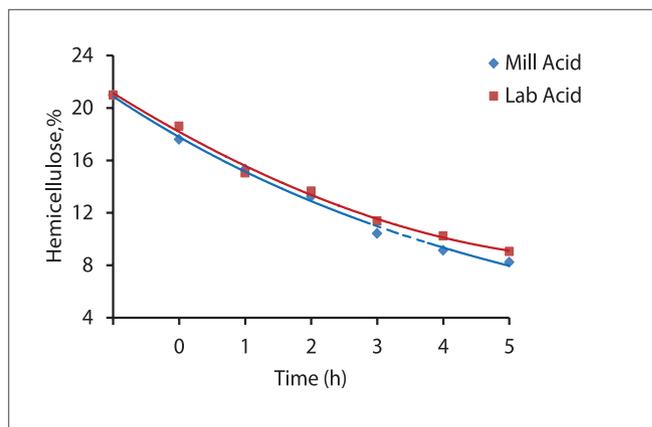


Figure 8. The hemicellulose content *versus* time for bisulfite cooking with either a mill or a lab prepared cooking acid. Conditions used: 154 °C

Table 6. The relative kinetic effect of the temperature for bisulfite pulping of spruce using lab acid is compared with the reference cook at 154 °C. The reference cook corresponds to Table 5 data

Temperature, °C	142	154	165
Cellulose	0	0	0
Hemicellulose	Lower	0	Higher
Lignin	Lower	0	Higher
Thiosulfate	Lower	0	Higher

variable and a mill prepared cooking acid had a slightly negative influence on the delignification rate and the decomposition rate of the cooking acid.

CONCLUSIONS

The temperature during a bisulfite cook has been shown to significantly influence the delignification rate, but also the degradation rate of the hemicellulose and the cooking acid. However, the degradation of the cellulose was, due to its high crystallinity, insignificant during the first hours of the cook. The quality of the cooking acid used had an influence on the different reactions during the cook, thus the results from a lab cook with very pure and well defined cooking acid cannot completely forecast the results in a pulp mill where the cooking acid is contaminated with by-products and dissolved organic matter.

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REFERENCES

1. <http://www.pulpapernews.com/2014/05/domsj-fabriker-hits-production-record>
2. Deshpande, R.; Sundvall, L.; Grundberg, H.; Germgård, U. (August 2014): *The Initial phase of sodium bisulfite pulping of spruce, Part I*. Accepted for publication in "Cellulose Chemistry and Technology".
3. Annergren, G.; Croon, I.; Enström, B. E.; Rydholm, S. A. (1961): *On the Stabilization of Spruce Glucomannan in Wood and Holocellulose*. Svensk Papperstidning, 62 (10), p.388-389.
4. Annergren, G.; Rydholm, S. A. (1959): *On the Behaviour of Hemicelluloses during Sulphite Pulping*. Svensk Papperstidning, 62(20), p.738.
5. Annergren, G.; Rydholm, S. A. (1960): *On the stabilization of glucomannan in the pulping process*. Svensk Papperstidning, 63 (18), p.592-594.
6. Kaufmann, Z. (1951): *Über die chemischen Vorgänge beim Aufschluss von Holz nach dem Sulfite prozess*. ETH-Bibliothek, Zurich, Switzerland p.100.
7. Rydholm, S. A.; *Pulping Processes*, NY, USA: Wiley, ISBN 089874-856-9, p.510,95,96,467,507,112,530,535, (1965).
8. Rydholm, S. A.; Lagergren, S. (1959): *On the delignification Reaction of the Technical Sulphite Cook*. Svensk Papperstidning, 62(4), p.112,103,62.
9. Schöön, H.N. (1961): *The Reaction between Thiosulfate and Wood during Sulphite cooking-Part 1*. Svensk Papperstidning, 64(23), p.624.
10. Schöön, H. N. (1962): *Kinetics of the Formation of Thiosulfate, Polythionates and Sulfate by the Thermal Decomposition of Sulphite cooking liquor*. Svensk Papperstidning, 19, p.734, 737,975,976.
11. Sixta, H.; *Handbook of Pulp*, Wiley-VCH GmbH & Co, KG a A. Weinheim, Germany. ISBN:3-527-30999-3, p.392,406,418-420,423-424, (2006).
12. Sjöström, E.; Häggglund, P.; Janson, J. (1962): *Changes in the Liquor composition During Sulfite Pulping*. Svensk Papperstidning, 65(21), p.864-865.
13. Meier, H. (1958): *Studies on hemicelluloses from Pine*. Acta Chem, Scandinavia. 12(10), p.1911-1918.
14. Goldfinger, G. (1941): *Variation of the order and energy of activation of the delignification reaction in sulphite cooking*. Tappi Section - Paper Trade J, p.289-291.
15. Rusten, D. (1962): *Degradation of cellulose and solution of hemicelluloses during spruce sulfite pulping*. Norsk Skogindustri. Vol 16, p.328-339.
16. Fischer, K. I.; Schmidt. (1991): *Kinetics of cellulose and lignin degradation during the acid bisulfite process and the possibilities for cooking control*. Tappi J. 74(1), p.82-185.
17. Wu, S.; Argyropoulos, D. S. (2003): *An improved method for isolating lignin in high yield & purity*. Journal of Pulp Paper Sci. 29(7), p.235.
18. Be Miller, J.N. (1967): *Acid-catalyzed hydrolysis of glycosides*. Adv. Carbohydrate Chem. Vol 22, p. 25-108.

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