Kinetics of cellulose and lignin degradation during the acid bisulfite process and the possibilities for cooking control

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ABSTRACT *We have studied the kinetics of cellulose and lignin degradation at the liquor-to-wood ratio, the SO_2 concentration, and the temperature that predominate during the acid bisulfite process. Kinetic equations can be used to predict the end of the cooking period. The rate coefficients were considered independently of the cooking parameters. By continuous measurement of the color and conductivity, it is possible to determine the rate for the development of color and conductivity. These parameters can be used to control the pulping process.*

KEYWORDS
Acid bisulfite pulping
Cellulose
Chemical analysis
Delignification
Lignin
Kinetics

Hagberg and Schöön (*1*) studied the kinetics of lignin and hemicellulose and, in 1974, reported the formulas for lignin dissolution and hemicellulose dissolution during the acid bisulfite process to be:

$$-dL/dt = k_L(T)[L]^b[HSO_3^-]^\alpha[H^+]^\beta \quad (1)$$

$$-dh/dt = k_h(T)[h]^d[H^+]^\gamma \quad (2)$$

where

L = lignin

h = hemicellulose

t = time

k = rate constant

T = temperature in kelvin.

Although these kinetic models describe the processes well, they are too complicated to determine the concentration of hydrogen (H^+) and bisulfite (HSO_3^-) ions in practical use. In addition, these researchers employed ideal cooking conditions, rendering their derived exponent values inapplicable to the industrial process. The aim of our work was to extend the findings of Hagberg and Schöö to the industrial setting.

Kinetics of cellulose degradation

To model the decrease in pulp viscosity during the acid bisulfite process, it is not enough to know that the dissolution of carbohydrates depends on the concentration of hydrogen ions. Proper modeling of the decrease of pulp viscosity during the acid bisulfite process also requires an understanding of the parameters that influence the concentration of hydrogen ions.

The main factors influencing the reactions during the pulping process are the amount of pulping chemicals applied and the cooking temperature. The total amount of pulping chemicals is determined by the amount of cooking liquor used and the concentration of pulping chemicals in the cooking liquor. Therefore, we have studied the kinetics of cellulose and lignin at typical industrial values for the ratio of cooking liquor to wood, the concentration of sulfur dioxide (SO_2), and temperature.

Beech wood chips were pulped according to an acid bisulfite process using calcium as base in the cooking liquor, varying the liquor-to-wood ratio and the SO_2 concentration. (Throughout, the liquor-to-wood ratio is the ratio of the cooking liquor to the amount of oven-dry wood, not the ratio of the total liquor amount to the amount of wood chips.) The equations derived from these studies were tested for their ability to predict the end of the cooking period.

Influence of chemicals doses on hydrogen ion concentration

Table I shows correlation coefficients between the SO_2 concentration and the concentration of hydrogen ions at several cooking times. The concentration of hydrogen ions was calculated from the concentration of different ions in the cooking liquor with the help of the protolysis equilibrium of SO_2 and the electroneutrality relation. The

I. Coefficients of the correlations between the concentration of hydrogen ions and those of sulfur dioxide and strong acids (significance level = 0.05)

	Parameter: conc. of hydrogen ions					
		At 133°C				
Parameter	At 115°C	0 h	1 h	2 h	3 h	At the end
SO_2 concentration of cooking acid	0.99	0.91	0.90	0.71	0.73	0.81
At 115°C	0.97	0.93	0.87	0.61	...	0.68
At 133°C		0.94	0.84	...	...	0.60
After 1 h at 133°C			0.80	...	...	...
Conc. of strong acids						
After 1 h at 133°C			0.76	0.85	0.70	0.69
After 2 h at 133°C				0.89	0.73	0.74
After 3 h at 133°C					0.81	0.80
At end of the cook						0.87

... indicate that correlation values were below the required level.

II. Correlation coefficients between viscosity and ion concentrations

Cooking time, h	Correlation coef.	Ion
0	0.80	HSO^-_3
1	0.81	HSO^-_3
2	0.81	HSO^-_3
3	0.64	HSO^-_3
1	-0.62	H^+
2	-0.80	H^+
3	-0.76	H^+
(end)	-0.80	H^+

Temp. = 133°C.

concentrations of the strong acids—that is, the lignosulfonic acid and α-hydroxy sulfonic acids—were also determined. These measurements allowed us to examine the relationship between the concentration of hydrogen ions and strong acids (*2*).

The results show high correlations between the concentration of hydrogen ions and the SO_2 concentration of fresh cooking liquor up to 1 h at maximum temperature. Likewise, the SO_2 concentration of the cooking liquor during the first cooking steps correlated with the concentration of hydrogen ions up to 1 h at maximum temperature. Although the concentration of strong acids after 1 h at maximum temperature was low, an influence on the hydrogen ion concentration was already evident. In the course of the cooking process, the SO_2 concentration lost its impact on the hydrogen ion concentration, and the influence of the strong acids was strengthened.

Correlation coefficients between the liquor-to-wood ratio and hydrogen ion concentration were low, eliminating the liquor-to-wood ratio as a determinant of cellulose degradation. This finding suggests that the rate of cellulose degradation depends primarily on the concentrations of SO_2 and strong acids.

Influence of cooking acid parameters on the pulp viscosity

Next, we studied the relationship between the viscosities of the cooked pulps and the parameters of the cooking liquor during cooking. Viscosity was closely correlated with the liquor-to-wood ratio ($r = 0.78$) but not to the SO_2 concentration in the cooking acid. (These experimental data on viscosity vs. liquor-to-wood ratio and viscosity vs. SO_2 are not listed.) Furthermore, the results in **Table II** show that the concentration of bisulfite ions exerted a great influence on the pulp viscosity only at the beginning of the cook, but the influence of the concentration of hydrogen ions increased until the end of the cook.

Both the liquor-to-wood ratio and the concentration of hydrogen ions, then, affect the viscosity of the pulp. Therefore, wood was cooked at different liquor-to-wood ratios and with different SO_2 concentrations in the cooking liquor, and we determined the effect of these variables on the degradation of cellulose.

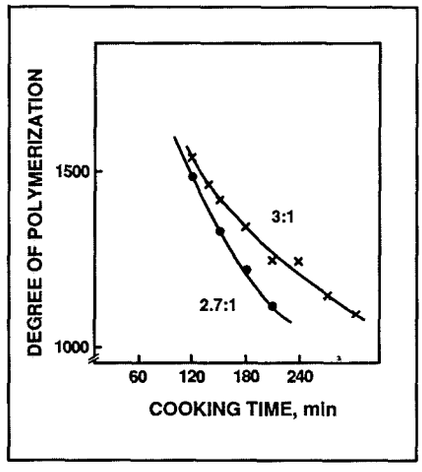
Figures 1 and 2 show the decrease in the degree of polymerization during pulping. Figure 1 shows the influence of the amount of cooking liquor. The degradation of cellulose begins at about the same time, but the cellulose degradation proceeds faster with less liquor added.

Figure 2 shows that with more SO_2 in the cooking liquor, the degradation of cellulose sets in earlier. However, the hydrolysis of the cellulose chains proceeds faster at the lower SO_2 concentration.

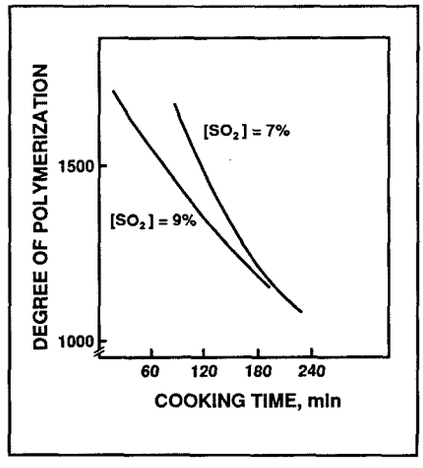
Modeling of the viscosity degradation

Because the degree of polymerization of cellulose does not diminish in accordance with a simple reaction order, the changes in the degree of polymerization had to be computed.

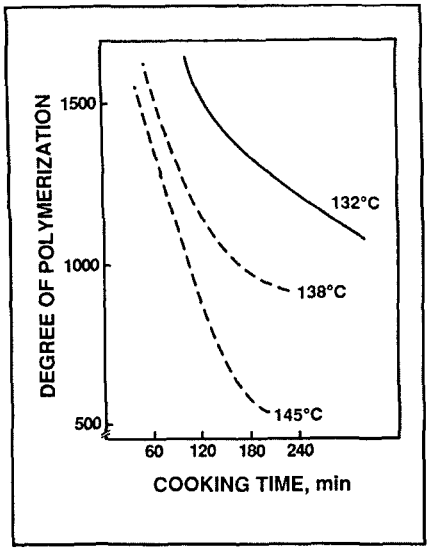
1. Changes of the degree of polymerization after reaching maximum temperature using different ratios of cooking liquor to wood; temperature 132°C



2. Changes of the degree of polymerization applying two different amounts of SO_2 in the cooking liquor



3. Changes of the degree of polymerization at different maximum temperatures



III. Pulping parameters and results of model testing for the degradation of cellulose

No.	Liquor-to-wood ratio	$[SO_2]$, %	Max. temp., °C	Cooking time, min	Viscosity, mPa·s	
					Required	Determined
1	2.5:1	6.5	133	207	24.6	24.9
2	2.5:1	7.5	132	171	35.5	35.2
3	2.7:1	7.5	132	190	35.8	35.0
4	2.7:1	8.5	133	245	22.3	23.3
5	2.9:1	8.5	131	222	36.8	37.1

We found that the degree of polymerization does not change according to a simple reaction order, but the number of scissions taking place does. Thus, the degradation of cellulose can be described by the following rate law:

$$dS/dt = k_s \times e^{-E_s/T} \quad (3)$$

where

E_s = activation factor

S = the number of scissions

k_s = rate constant.

The number of scissions rises according to a reaction of zero order, but nevertheless the rate of scissions depends on the amount of chemicals used. Therefore, the rate coefficient k_S was determined to be dependent on the amount of cooking liquor used and its concentration of SO_2.

The studies were carried out according to a statistical test plan that was evaluated with reference to the kinetic behavior of the cellulose. The pulps were produced at a liquor-to-wood ratio (x_1) varying from 2.5:1 to 2.9:1 and at an SO_2 concentration in the cooking liquor (x_2) ranging from 6.5% to 8.5%. The rate coefficient can be calculated according to the following equation:

$$k_S = 2.683 \times 10^{-6} - 0.151 \times 10^{-6}x_1 + 0.152 \times 10^{-6}x_1^2 - 0.138 \times 10^{-6}x_2^2 \quad (4)$$

Influence of cooking temperature

Beech chips were pulped at a liquor-to-wood ratio of 3:1, at an SO_2 concentration in the cooking liquor of 7%, and at maximum temperatures of 132°C, 138°C, and 145°C.

Figure 3 shows the diminution of the degree of polymerization during cooking at different maximum temperatures. This figure shows an increased degradation of cellulose and an earlier beginning of degradation at rising maximum temperature.

By using the Arrhenius relation, we determined an activation factor for the degradation of cellulose of E_S = 21,170 K at a correlation coefficient of $r = 0.997$.

Results of model testing

The model equation for calculating the cellulose degree of polymerization during pulping is:

$$dS/dt = k_S(T) = k_S \times e^{-E_s/T} \quad (5)$$

where k_S is a function of the liquor-to-wood ratio and the SO_2 concentration.

From Eq. 2, the required cooking time for a certain degree of polymerization can be calculated if the liquor-to-wood ratio, the SO_2 concentration, and the maximum temperature are known.

$$t_E = (S_E - S_0)/k_S + t_0 \quad (6)$$

where

t_E = calculated cooking time to reach S_E

S_E = degree of scissions required in the pulp

S_0 = number of scissions at t_0

t_0 = the time at which maximum temperature is reached.

According to this equation, the cooking times for the required pulp viscosities were calculated with respect to different cooking conditions. **Table III** shows the cooking conditions required and the viscosities as determined. The results show a good agreement between the required pulp viscosities and the viscosities of the pulp cooked according to the calculated conditions.

Using the color and conductivity of the cooking liquor for pulping control

To determine whether the pulping process can be monitored and controlled during the cooking time, some evaluations must be made concerning the parameters. Can the color and conductivity of the cooking liquor reflect the process adequately, and are they suitable for process control?

Modeling the development of color

By continually measuring the color under the available pressure and the actual temperature, it is possible to determine on an on-going basis the rate for the development of the color. The rate for developing color depends on the liquor-to-wood ratio. After determining the activation factor, we can use the following equation to calculate the color of the cooking liquor in advance:

IV. Pulping parameters and results of model testing for the development of color

Liquor-to-wood ratio	$[SO_2]$, %	Max. temp., °C	Cooking time, min	Color absorbance	
				Required	Determined
2.5:1	6.5	133	207	82.9	86.0
2.5:1	7.5	132	171	69.6	71.0
2.7:1	8.5	133	245	84.1	83.5
2.9:1	8.5	131	255	76.2	75.0

$$dC/dt = k_C \times e^{-E_C/T} \quad (7)$$

where

E_C = 11,000 K

C = color development.

After integrating the equation, the cooking time for reaching the required viscosity is used to calculate the color that will be obtained at the end of the cook. The color at the beginning of the cook can be measured.

Table IV shows the results obtained in model testing.

Modeling the conductivity

The conductivity of the cooking liquor recorded at cooking pressure and temperature shows a characteristic development (**Fig. 4**).

At maximum temperature, the conductivity of the cooking liquor drops because the pulping chemicals react with wood up to a certain point. At this point, the formation of ions, especially hydrogen ions, and the consumption of ions are in equilibrium, and the conductivity does not vary. If the concentration of the ions formed rises by dissolution of such reaction products as lignosulfonates and α-hydroxysulfonic acids, the conductivity of the cooking liquor increases. The rise in conductivity may also be used for calculating the end point of cooking. The rate of the increase in conductivity depends on the liquor-to-wood ratio, the SO_2 concentration in the cooking liquor, and the temperature.

$$d_{\alpha e}/dt = k_{\alpha e} \times e^{-E_{\alpha e}/T} \quad (8)$$

Kinetics of lignin dissolution

According to Hagberg and Schöön (*1*), the concentrations of hydrogen ions and bisulfite ions control the kinetics of lignin degradation. Both parameters can be determined only using complicated technical equipment. Therefore, we turn to the possibility of modeling lignin degradation via measurable parameters such as liquor-to-wood ratio and temperature.

Studies have shown that the proportion between the quantities of acid-soluble lignin and acid-insoluble lignin changes in the impregnation phase (*3*). We determined these proportions according to the Klason method. At maximum temperature, both the acid-insoluble lignin and the acid-soluble lignin in the pulp are reduced (*3*).

Figure 5 shows the dissolution of lignin during the cooking phase at maximum temperature. The content of lignin approaches a minimum concentration, and the portion of lignin remaining in the pulp and determined as acid-insoluble lignin diminished like a second-order reaction.

Influence of SO_2 dosage on the permanganate number

To evaluate the dissolution of lignin, we used the permanganate numbers instead of the lignin content of the pulps. **Figure 6** shows the changes in the permanganate number during the cooking phase at maximum temperature. The cooks were carried out with liquors at concentrations of 7% SO_2 and 1.05% CaO and 9% SO_2 and 1.09% CaO, respectively. The liquor-to-wood ratio was 2.7:1. By applying higher SO_2 concentrations in the cooking liquor, the lignin dissolution begins earlier than with a cooking liquor having a lower SO_2 concentration. At the same time, under the conditions of maximum temperature, more lignin is dissolved using a cooking liquor with a higher SO_2 concentration. Furthermore, the SO_2 concentrations in cooking liquors diminish. in a parallel course but on different levels.

The calculation of the reaction order showed a decrease both of the permanganate number and of the SO_2 concentration in the cooking liquor according to a second-order reaction. The rate coefficient of the change of the permanganate number, *PN*, and that of the diminution of the SO_2 concentration depends on the SO_2 concentration of the cooking liquor at the start of the cook:

$$-dPN/dt = k_{PN} \times PN^2 \times [SO_2]^2 \quad (9)$$

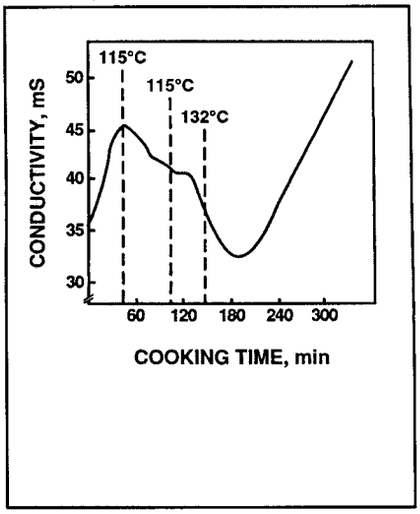
with E_{PN} = 10,953 K. The rate factor was k_{PN} = 0.001451 at 132°C.

The decrease of SO_2 is characterized by the following kinetics equation:

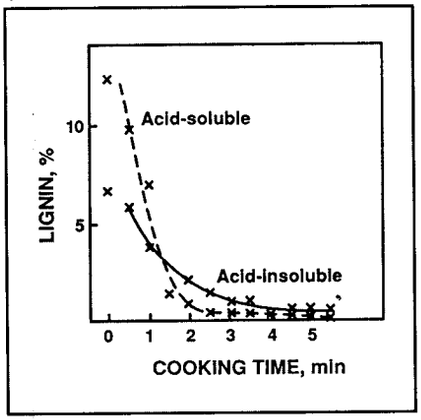
$$-d[SO_2]/dt = k_{SO_2} \times [SO_2]^{1.5} \quad (10)$$

With these kinetics equations, the changes in the permanganate number and SO_2 concentration during the cook can be calculated.

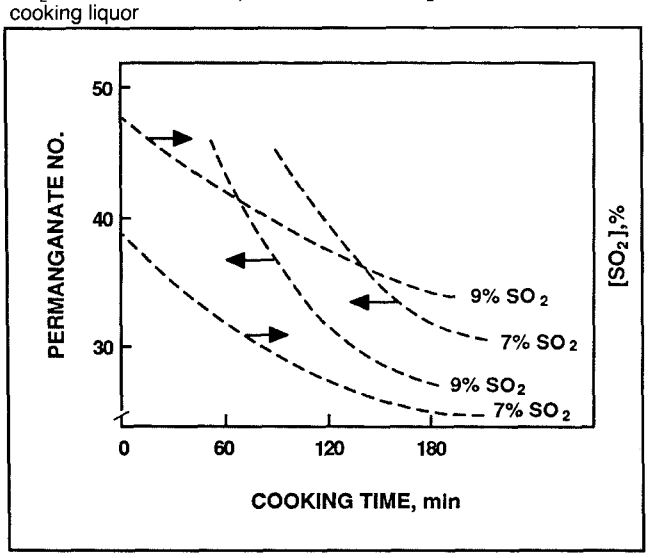
4. Development of conductivity of liquor found by continuous measurements under available pressure and temperature



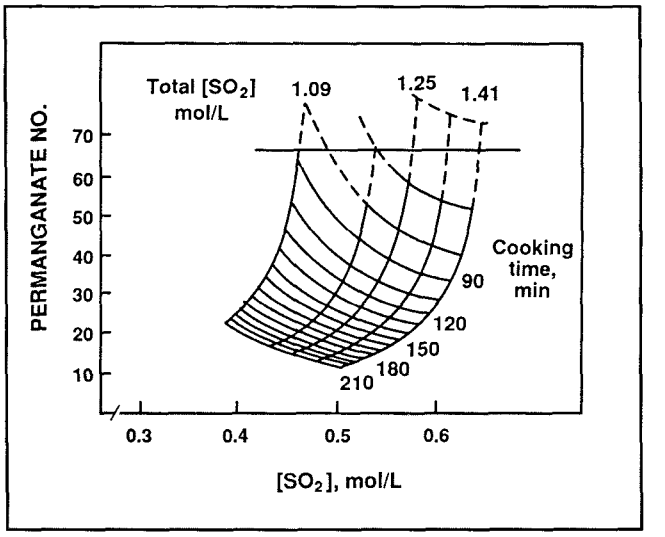
5. The changes of acid-soluble and acid-insoluble lignin in pulps during the cooking phase



6. The changes of the permanganate number of the pulp and the SO_2 concentration of liquor at different SO_2 concentrations in the cooking liquor



7. The decrease in the permanganate number and the SO_2 concentration of the cooking liquor



Using SO_2 concentration to control the cook

Figure 7 shows that the use of more SO_2 in the cooking liquor considerably accelerates delignification, and leads to a lower permanganate number, but for reaching the same level of permanganate number, no more SO_2 is consumed. The relationship between the permanganate number and the diminution of the SO_2 concentration in the cooking liquor is close enough to use the SO_2 concentration to control cooking.

To validate this goal, we needed to determine the influence of the liquor-to-wood ratio. Using a statistical test plan, we determined the dependence of the rate coefficient on the liquor-to-wood ratio and the initial SO_2 concentration. The results showed that the rate coefficient for the diminution of SO_2 in the cooking liquor depends on the liquor-to-wood ratio and on the SO_2 concentration at the beginning of the cook. Because these parameters could be fixed, it is possible to control the delignification of the pulp based on the SO_2 concentration in the cooking liquor.

Final remarks

Our purpose was to develop a practicable model for controlling the viscosity of pulp and for observing the viscosity decrease with the help of parameters that are measurable during the cooking phase. The results of laboratory test runs have shown a satisfactory agreement between (a) the calculated and the determined pulp viscosities and (b) the conductivity and the color as determined by the control sensors. Further studies are needed to prove how suitable it is to apply these models on the industrial scale.□

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