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Measuring and Controlling Model of Pulp Kappa Number with Spectroscopy during Batch Sulfite Pulping Process

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Aiming at the difficulties and problems of online measurement of pulp kappa number during batch pulping, this paper proposes a new measuring idea, which is to predict the lignin content in pulp through the measurement of dissolved lignin in cooking liquor with spectral technology. The basic and modified mathematical model of kappa number during sulfite pulping as well as the end point controlling model are put forward in detail. The site running result shows that the introduction of modified factor ε , which represents the change of the total lignin amount added into the digester, is effective. Therefore, the online measurement of kappa number and the determination of the end point of pulping can be achieved.

1. Introduction

Kappa number is an important quality index of pulp; it indicates the cooking degree of raw material in the pulping process, and it is a key parameter for pulping process control. The constant kappa number will maximize product yield and pulp quality while minimizing consumption of energy and chemicals. Therefore, measuring and controlling of the pulp kappa number are the key factors for a pulp mill to improve product quality and decrease the costs of products. However, it is well-known that it is almost impossible to know the kappa number through wet chemical analysis of pulp during batch pulping because pulping is carried out under high-temperature and high-pressure conditions.

Some attempts in development of instrumental methods for online prediction of the kappa number have been reported in the literature. An instrument for online kappa number determination has been developed on the basis of the ultraviolet absorption of pulp and was reported to be successful.¹ Bobier et al. reported that the ultraviolet absorption of cooking waste liquor at 2050 Å could be used to indicate the extent of delignification.² Although Bobier² reported good linear correlations, Michael et al. were unable to reproduce the results with the same degree of confidence.³ A method for the determination of cellulosic-fiber properties, such as the residual lignin content of chemical pulp, with the aid of a spectroscopic technique obtained over a range covering the visible and the near-IR regions of the electromagnetic spectrum, has been developed.⁴ Another new method for online measurement of pulp kappa number by means of near-IR diffuse reflectance spectroscopy of pulp and support vector machine (SVM) modeling has been developed.⁵ An inferential method used a mathematical model with online liquor analysis to predict the lignin content of pulp every 5 min. Conductivity, ion chroma, refractive index, and UV absorbance analysis of cooking liquor were used to measure effective alkali, sulfide consistency, total solids, and the lignin content of the cooking liquor.^{6–8} A spectrophotometric method was developed for rapid pulp kappa number measurements under strongly acidic reaction conditions. The pulp kappa number was derived from the ratio of the absorption spectral intensities at a

specific wavelength measured at the beginning and end of the reaction of the pulp with permanganate.^{9–11}

The analyzing samples of the above measuring technologies are separate pulps or cooking liquors. Although the commercial analyzer of kappa number has been reported successfully in the bleaching process, the maintaining accessory and calibration accessory are necessary for the sake of accuracy, and it is not suitable for batch pulping because of the analyzing sample. In addition, ultraviolet absorption has been investigated at 280 and 205 nm for dissolved lignin, but in both cases the absorbance changes much less in the last cooking phase than that of visible light, which is therefore most suited.

In this paper, aiming at the difficulties and problems of online measurement of pulp kappa number during batch pulping, we propose a new measuring idea, which is to predict the lignin content in pulp through the measurement of dissolved lignin in cycled cooking liquor with spectral technology during batch pulping. Therefore, the online measurement of the kappa number can be achieved. On the basis of the new idea, the basic measuring model, the modified basic model of pulp kappa number, and the end point controlling model of sulfite pulping with spectral technology have been developed. In the last, the validation of the measuring model and the end point controlling model for sulfite pulping are also given. The study would provide basis for online measurement of kappa number and quality control for the pulping process.

2. New Measuring Idea of the Pulp Kappa Number

According to the arts of batch pulping, the total lignin amount in the digester is ascertained during pulping. It is well-known that the lignin content in the wood decreases while the lignin content in the liquor increases during pulping, and the pulp kappa number indicates the lignin content retained in the pulp. Although it is difficult to take out a pulp sample during batch pulping, it is easy to get a sample from recycling cooking liquor. Therefore by the reverse method, prediction of the lignin content retained in the pulp can be achieved through the dynamic measuring of the lignin content in the cooking liquor during pulping with spectral technology, and the online measurement of pulp kappa number can be expected. The key point of the new measuring idea is, can lignin content retained in the pulp be expressed by the lignin content dissolved in the cooking liquor? This is the important factor we must be concerned with.

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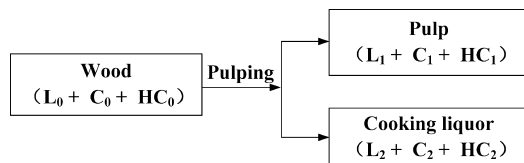


Figure 1. Transferring diagrammatic sketch of wood component during pulping.

In the pulping process, the substances in wood transfer into the cooking liquor without ceasing. The transfer course is illustrated in Figure 1.

According to the fundamental mass conservation law, we have

$$L_0 = L_1 + L_2 \quad (1)$$

On the basis of the definition of the pulp kappa number, Ka , there should be some direct relation between the pulp kappa number and the lignin content in the pulp:

$$Ka = f(L_1) = f(L_0 - L_2) \quad (2)$$

From the new measuring idea, the sample has been changed from pulp to cooking liquor, which is easy to get, and the spectrum absorption theory can be applied to measure the lignin content in the cooking liquor.

3. Measuring Model of Sulfite Pulp Kappa Number

3.1. Development of the Basic Model. According to Beer–Lambert's law,

$$A = \log\left(\frac{I_0}{I}\right) = kcb \quad (3)$$

In eq 3, if “ c ” represents the lignin consistency in the cooking liquor during pulping, then

$$L_2 = V \frac{A}{kb} \quad (4)$$

Many investigations^{12,13} have proved that the lignin content in pulp has a good linear relation with the pulp kappa number. From eqs 1 and 4 we can get

$$\begin{aligned} Ka &= \frac{L_1}{\eta} = \frac{L_0 - L_2}{\eta} = \frac{L_0 - (V/kb)A}{\eta} \\ &= -\frac{V}{kb\eta}A + \frac{L_0}{\eta} \end{aligned} \quad (5)$$

Equation 5 means that, during pulping, Ka is related to the absorbance A of the cooking liquor, the total lignin amount L_0 added into the digester, and the volume V of the cooking liquor in the digester as well. Calibration of eq 5 is necessary since the density and hue of the cooking liquor varies with the base and the wood species.

From the pulping conditions and with the help of a flow transmitter, V of the cooking liquor in the digester can be preserved as constant technologically. But, controlling L_0 added into the digester is not an easy job. Accounting for the change of L_0 , what would eq 5 be?

3.2. Modification of the Basic Model. If L_0 added into the digester could be kept constant, eq 5 would be simplified to

$$\begin{aligned} Ka &= -\frac{V}{kb\eta}A + \frac{L_0}{\eta} \\ &= -\frac{V}{kb\eta}A + B \end{aligned} \quad (6)$$

where $B = \bar{L}_0/\eta$ and B is a constant.

Equation 6 means that if the total lignin amount added into the digester could be kept constant, then Ka has a linear relation with A of the cooking liquor.

On the other hand, accounting for the change of L_0 added into the digester, a modified factor ε was introduced. Then eq 5 is changed to

$$\begin{aligned} Ka &= -\frac{V}{kb\eta}A + \frac{L_0}{\eta} \\ &= -\frac{V}{kb\eta}A + \frac{\varepsilon \bar{L}_0}{\eta} \\ &= -\frac{V}{kb\eta}A + \varepsilon B \end{aligned} \quad (7)$$

The practical sulfite pulping experience tells us that the rising rate s of SO_2 pressure in the digester during the second temperature rising stage of pulping can reflect the change of L_0 added into the digester (Figure 2).

The more raw material added into the digester, the more cooking liquor consumed, the slower rising the rate of SO_2 pressure is, and the more difficult pulping is.¹⁴ The rising rate of SO_2 pressure in the digester has an inverse relation with L_0 added into the digester. The calculation of modified factor ε is

$$P'_{\text{SO}_2} = P' - P_{t1} \quad (8)$$

$$P''_{\text{SO}_2} = P'' - P_{t2} \quad (9)$$

$$s = \frac{d(P_{\text{SO}_2})}{dt} = \frac{P'_{\text{SO}_2} - P''_{\text{SO}_2}}{t} \quad (10)$$

$$\varepsilon = \frac{L_0}{\bar{L}_0} = \frac{\bar{s}}{s} \quad (11)$$

So, if the absorbance of the cooking liquor could be measured during pulping, and the calculated modified factor ε is used in eq 7, the prediction of Ka would be realized.

4. End Point Controlling Model of Sulfite Pulping

As we know, the end point of pulping is very important, which affects the production and quality of pulp directly. The terminal aim of online measurement of pulp kappa number is to determine the end point of pulping properly and produce qualified pulp. So, it is necessary to develop the end point controlling model of pulping.

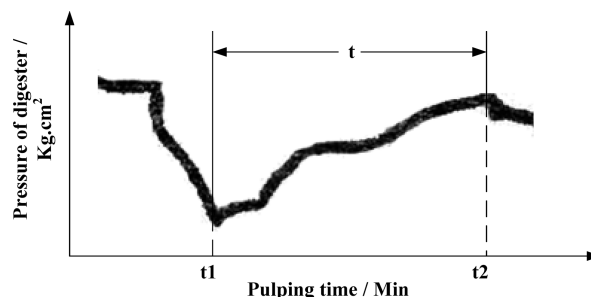


Figure 2. Partial enlarged graph of digester pressure curve of sulfite pulp mill.

According to the kinetics theory of sulfite pulping,¹⁴ the delignification rate equation could be written:

$$\begin{aligned}\frac{dL_1}{dt} &= -k(P_{\text{SO}_2})^{0.75} \\ &= -k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75}\end{aligned}\quad (12)$$

where $P_{\text{SO}_2} = P - P_s$.

From eq 12 we have

$$dL_1 = -k(P_{\text{SO}_2})^{0.75} dt \quad (13)$$

$$\int_{L_0}^{L_1} dL_1 = -\int_0^t k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt \quad (14)$$

$$L_1 - L_0 = -\int_0^t k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt \quad (15)$$

$$L_0 = L_1 + \int_0^t k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt \quad (16)$$

As stated before

$$B = \frac{\bar{L}_0}{\eta} \quad (17)$$

if we take eqs 5 and 17 into eq 16, then

$$\begin{aligned}L_0 &= \eta Ka + \int_0^t k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt \\ &= \varepsilon \eta B\end{aligned}\quad (18)$$

where “ ηKa ” represents the lignin content retained in pulp; the second part of eq 18 represents the lignin content dissolved in the cooking liquor.

From eq 18 we have

$$\int_0^t k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt = \eta(\varepsilon B - Ka) \quad (19)$$

and define

$$D = \int_0^t k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt \quad (20)$$

then

$$\begin{aligned}D &= \int_0^t k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt \\ &= \eta(\varepsilon B - Ka)\end{aligned}\quad (21)$$

where D is the delignification factor of sulfite pulping, we name it the D factor, which is related to the pulping temperature T , the SO_2 pressure in the digester P_{SO_2} , the pulping time t , and the raw material.

To produce uniform pulp, if the target pulp kappa number at the end point is Ka_e , then

$$D_e = \eta(\varepsilon B - Ka_e) \quad (22)$$

$$D_e = \int_0^{t_e} k_0 e^{-E/RT} (P_{\text{SO}_2})^{0.75} dt \quad (23)$$

Equation 22 is the end point controlling model of pulping. It means that if the Ka_e is known, then the corresponding D value D_e at the end point of pulping can be calculated. Using eq 23, measuring T and P_{SO_2} , the terminal time of pulping t_e can be calculated and the end point determination of pulping can also be realized.

5. Validation of Measuring and End Point Controlling Model for Sulfite Pulping

5.1. Sulfite Cooking of Pulp Mill. Pulpings were carried out with a batch type digester (100 m³) with cooking liquor recycling in Guangzhou Paper Mill. Chips of Masson's pine were used in this experiment. The chips were screened before pulping. The pulping condition was as follows: $\text{Ca}(\text{HSO}_3)_2$ based cooking liquor; total acid (TA), 6.43%; combined acid (CA), between 1.0 and 1.25%. The highest pulping temperature is 138–139 °C. The liquor to wood ratio is 4:1. The cooking curve of the pulp mill is illustrated in Figure 3.

5.2. Kappa Number Determination by Titration. After the batch pulping, pulps were washed thoroughly and screened. Their kappa numbers were analyzed according to the Tappi Testing Method.¹⁵

5.3. Visible Spectra Determination. Close to the end of pulping, spent liquor was sampled and cooled at once. Then, samples were pretreated by filtration with a micropore filter (0.45 μm). The visible spectra were determined by an ultraviolet–visible spectrometer, Shimadzu-2201.

5.4. Results and Discussion. After analyzing the spectrograms of the cooking liquor, saccharide (including glucose, xylose, mannose), water, and sulfonated lignin with the spectrophotometer, considering the smoothing of absorption spectrum and the relationship between absorbance and the relative error of the measurements, the visible wavelength range (460–580 nm) for prediction of pulp kappa number has been determined, in which the absorption of the cooking liquor mainly comes from the lignin-sulfonate, while xylose, mannose, glucose, and water in sulfite cooking liquor had no obvious absorption in this wave range. Therefore, through the measurement of absorbance of the cooking liquor, the pulp kappa number (residual lignin content) could be predicted online during pulping.

On the basis of modeling studies in the laboratory, the kappa number measuring models have been applied in the sulfite pulp mill (Figure 4).

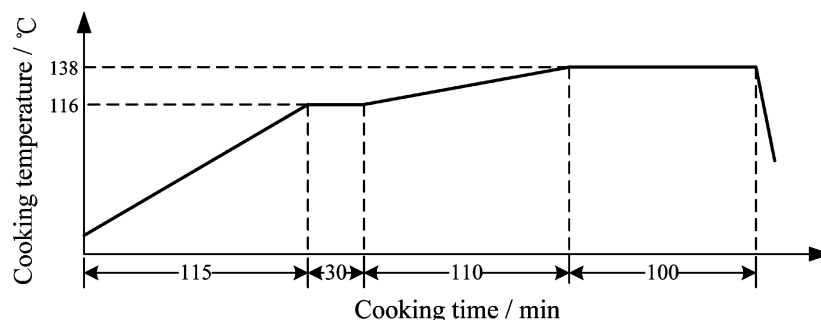


Figure 3. Sketch map of cooking curve of sulfite pulp mill.

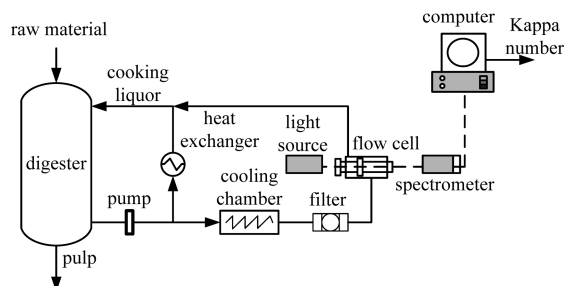


Figure 4. Schematic diagram of site running optical pulp kappa number measuring system.

Table 1. In-Situ Predicting Accuracy Tests of the Sulfite Pulp Kappa Number

sample no.	A^a	s	ε	$Ka(D)$	$Ka(P)$	ΔKa	$Ka(P)_m$	ΔKa_m
1	0.433	1.345	0.9890	17.98	17.74	-0.24	17.48	-0.50
2	0.390	1.404	0.9474	18.41	18.32	-0.09	17.08	-1.33
3	0.445	1.325	1.0037	17.65	17.57	-0.08	17.66	0.01
4	0.362	1.424	0.9343	18.12	18.70	0.58	17.15	-0.97
5	0.571	1.266	1.0506	17.65	15.86	-1.79	17.05	-0.60
6	0.444	1.379	0.9643	17.36	17.59	0.23	16.74	-0.62
7	0.309	1.419	0.9375	18.65	19.42	0.77	17.94	-0.71
8	0.321	1.374	0.9677	18.32	19.26	0.94	18.50	0.18
9	0.371	1.355	0.9818	17.41	18.58	1.17	18.15	0.74
10	0.358	1.384	0.9609	16.02	18.76	2.74	17.83	1.81
11	0.504	1.325	1.0037	17.65	16.77	-0.88	16.86	-0.79
12	0.668	1.276	1.0425	18.08	14.54	-3.54	15.55	-2.53
13	0.424	1.330	1.0000	18.79	17.86	-0.93	17.86	-0.93
14	0.577	1.281	1.0385	17.36	15.78	-1.58	16.69	-0.67
15	0.497	1.335	0.9963	16.59	16.87	0.28	16.78	0.19
16	0.428	1.340	0.9926	18.22	17.80	-0.42	17.63	-0.59
17	0.646	1.325	1.0037	16.59	14.84	-1.75	14.93	-1.66
18	0.385	1.355	0.9818	18.08	18.39	0.31	17.96	-0.12
19	0.363	1.379	0.9643	16.55	18.69	2.14	17.84	1.29
20	0.533	1.286	1.0345	16.93	16.38	-0.55	17.19	0.26
21	0.339	1.374	0.9677	17.17	19.01	1.84	18.25	1.08
22	0.456	1.320	1.0075	18.84	17.42	-1.42	17.60	-1.24
SE						1.45		1.01

^a A: The absorbance of cooking liquor was determined at a wavelength of 550 nm.

According to eqs 7 and 11, we should introduce a modified factor ε to modify the change of L_0 added into the digester. The average rising rate \bar{S} of SO_2 pressure in the digester was obtained from the analysis of practical data. During our experimental period, the average rising rate was

$$\bar{S} = 1.33 \text{ kg}/(\text{cm}^2 \cdot \text{h})$$

According to eqs 8–11 and Figure 2, if the total pressures in the digester P' , P'' and steam pressures in the digester P_{t1} , P_{t2} at times t_1 , t_2 could be measured, and the time t during the second temperature rising stage could be calculated as well, then the modified factor ε can be obtained.

From the modified factor ε being put into the basic kappa number measuring model, the results are shown in Table 1 and Figure 5.

We can see that using the modified factor ε representing the effect of L_0 of the raw material in the digester has really improved the predicting accuracy of the pulp kappa number. The predicted kappa number with a modified model is much closer to the determined kappa number. Therefore, the introduction of modified factor ε is effective.

6. Conclusions

Aiming at the difficulties and problems of online measurement of the pulp kappa number during batch pulping, this paper

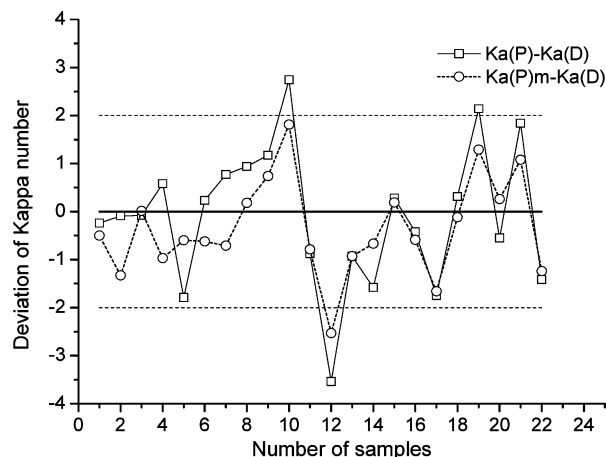


Figure 5. Comparison of pulp quality in the cooking end point with basic and modified models.

proposes a new measuring idea, which is to predict the lignin content in pulp through the measurement of dissolved lignin in cooking liquor with spectrum technology. The basic and modified mathematical models of the kappa number during sulfite pulping as well as the end point controlling model are put forward in detail. The site running result shows that the introduction of modified factor ε , which represents the change of the total lignin amount added into the digester, is effective. The predicted kappa number with the modified model is much closer to the determined kappa number. Therefore, the online measurement of pulp kappa number and the determination of the end point of pulping can be achieved.

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Nomenclature

- A = absorbance of cooking liquor
- C_0 = cellulose content in wood (g/kg)
- C_1 = cellulose content retained in pulp (g/kg)
- C_2 = cellulose content dissolved in cooking liquor (g/kg)
- c = lignin consistency in cooking liquor during pulping (mol/L)
- D = delignification factor of sulfite pulping
- D_e = delignification factor at the end point of pulping
- HC_0 = hemicellulose content in wood (g/kg)
- HC_1 = hemicellulose content retained in pulp (g/kg)
- HC_2 = hemicellulose content dissolved in cooking liquor (g/kg)
- Ka = pulp kappa number
- Ka_e = target pulp kappa number at the end of pulping
- $Ka(D)$ = kappa number determined by titration method
- $Ka(P)$ = kappa number predicted with basic model
- $Ka(P)_m$ = kappa number predicted with modified model
- ΔKa = absolute error of kappa number predicted with basic model, $\Delta Ka = Ka(P) - Ka(D)$
- ΔKa_m = absolute error of kappa number predicted with modified model, $\Delta Ka_m = Ka(P)_m - Ka(D)$

L_0 = lignin content in wood (g/kg)

\bar{L}_0 = calculated lignin amount which should be added into the digester according to the normal pulping condition (g/kg)

L_1 = lignin content retained in pulp (g/kg)

L_2 = lignin content dissolved in cooking liquor (g/kg)

P = total pressure in digester (kg/cm²)

P_s = steam pressure in digester (kg/cm²)

P_{SO_2} = SO₂ pressure in digester during sulfite pulping (kg/cm²)

s = actual rising rate of SO₂ pressure in digester during sulfite pulping (kg/cm²·min)

\bar{s} = rising rate of SO₂ pressure in digester during normal sulfite pulping (kg/cm²·min)

SE = standard error of predicted kappa number

t = pulping time (min)

t_e = terminal time of pulping (min)

T = pulping temperature (K)

V = volume of cooking liquor in digester (m³)

Greek Symbols

η = a constant relating to pulping raw material

ε = modified factor reflecting the change of the total lignin amount L_0 added into the digester

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