A Dissolved Lignin Monitoring-based Model for End-point Control during Displacement Kraft Pulping

Li-Ping Xin,[a,b,*] Bo Yu,[a] and Yuguo Zhou [a]

A novel mathematical model is reported for end-point control during displacement kraft pulping. The model was based on an on-line process that measured the dissolved lignin content in cooking liquor using an attenuated total reflection ultraviolet spectroscopy method that had been developed previously, from which a relationship between the pulp kappa number and integrated dissolved lignin content was established. The results showed that there was good agreement between the pulp kappa numbers measured by the presented model and TAPPI standard method. The presented method is straightforward and accurate and has the potential for on-line process control in mill operation.

*Contact information: a: School of Information and Control Engineering, Qingdao University of Technology, Qingdao, Shandong, China; b: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China; *Corresponding author: lpxin@qut.edu.cn*

INTRODUCTION

Presently, kraft pulping (using NaOH and Na_2S as the cooking agents) is the dominant process worldwide for the production of chemical pulps (Brown 2014). Among the kraft pulping methods, displacement cooking (*i.e.* SuperBatch, Enerbatch, and Rapid Displacement Heating) has a number of advantages over conventional batch cooking, which is accomplished with a batch digester connected to multiple intermediate liquor holding tanks. The biggest advantage is that such cooking process options can avoid the extensive degradation of hemicelluloses/cellulose during the initial cooking phase caused by high alkalinity and the condensation of dissolved lignin on the pulps at the end of cooking caused by low alkalinity (Sixta 2006). In kraft pulping, the pulp kappa number represents the degree of delignification and is an important parameter for determining the cooking end-point (Pelzer *et al.* 2013). But there is difficulty in realizing a real-time determination of the pulp kappa number. Because of the pulping process with high temperature and high pressure, it is almost impossible to sample from the pressure-tight digester. Therefore, an effective model for determining the end-point during displacement kraft pulping is highly desired.

Currently, there are many models available for the prediction of pulp kappa numbers during conventional batch cooking processes (Vroom 1957; Chari 1973; Hatton 1973; Tasman 1981; Christensen 1982; Gustafson *et al.* 1983; Kesavan *et al.* 2000; Lee and Bennington 2007). Because of the complexity of the fundamental models (Tasman 1981; Christensen 1982; Gustafson *et al.* 1983), empirical or semi-empirical models (Vroom 1957; Chari 1973; Hatton 1973; Kesavan *et al.* 2000) based on the initial chemical charges (*i.e.*, concentration of hydroxide and sulfide), H-factors (time and energy integrated parameter), and pulping raw material are typically adopted in mill applications.

However, the major problem of these models is their feasibility because the raw pulping material uniformity (*e.g.* the diversity of wood species and tree-age) has a notable impact on the accuracy of the pulp kappa number prediction (Santos *et al.* 2015). Therefore, models based on the on-line monitoring of the concentrations of chemical parameters, such as residual alkali, sulfide, and dissolved lignin in the cooking liquor, have been developed (Kerr 1976; Michell 1990; Venkateswarlu and Gangiah 1992; Vanchinathan and Krishnagopalan 1995; Masura 1999; Saucedo and Krishnagopalan 2000). These models provide more reliable pulping control because the changes in these chemical parameters have direct connections to delignification. Unfortunately, there are currently no chemical monitoring-based models available for displacement batch pulping because such cooking systems are more complicated than conventional batch cooking systems. Instead, pulping control in displacement batch cooking systems is mainly based on measuring the pulp kappa number by either on-line sensors (Faix *et al.* 1988; Chai *et al.* 2000; Trung *et al.* 2009) or an off-line titration method (T 236 om-99 1999) at the washing stage after the termination of pulping. As such, the kappa number information obtained from these methods has such a major time-tag that it is usually measured too late for use in controlling the pulping process. Moreover, although the kappa number information might be helpful for a feedback control mode, these methods fail to determine where the raw materials (wood species and compositions) vary remarkably (Faix *et al.* 1988; Chai *et al.* 2000; Trung *et al.* 2009; T 236 om-99 1999). Therefore, the development of a real-time model for end-point control in a displacement kraft pulping system is highly desired.

In this study, a new model was developed for end-point control during the batch displacement kraft pulping process with yellow bamboo. The model was based on on-line monitoring of dissolved lignin in the cooking liquor from three different stages: impregnation, hot displacement, and heating/cooking. The main focuses were to find the relationship between the pulp kappa number and integrated dissolved lignin content in the cooking liquor, the establishment of a dissolved lignin-based model for predicting the pulp kappa number, and application of the model in a lab-scale displacement kraft pulping process. The present model is straightforward and accurate and has great potential to be adopted for on-line process control in mill operations.

EXPERIMENTAL

Materials

The pulping chemicals, NaOH and Na_2S, were purchased from commercial sources. The yellow bamboo chips (approximately 30 mm × 20 mm × 4 mm) were obtained from the Jinghong bamboo forest in Yunnan province, China, from bamboo approximately three years old. The chips were washed and then air-dried at room temperature.

Apparatus

A lab-scale digester (10 L, 2110-2, Greenwood, Kansas, USA) system with three custom-made 5-L pressurized tanks containing warm black liquor (WBL, Tank A), hot black liquor (HBL, Tank B), and hot white liquor (HWL, Tank C) was used during displacement pulping. The pressurized tanks had the capability for not only heating the cooking liquor to the desired temperatures, but also injecting the liquor into the digester by the metering pump to displace some portion of the cooking liquor in the digester at different cooking stages.

bioresources.com

An ultraviolet (UV) spectrophotometer (UV-8453, Agilent, Palo Alto, USA) equipped with a peristaltic pump (RP-1, Rainin, Oakland, CA, USA), some tubing and connectors, and an attenuated total reflection (ATR) flow-cell (TNL-120H23-3, Axiom, New York, USA) was used to monitor the lignin in the cooking liquor at selected locations. The spectral data of the dissolved lignin was recorded by a computer.

Pulping Process

During the pulping process, 1.2 kg of yellow bamboo chips (oven-dried) were placed in the digester. The white liquors were prepared using NaOH and Na_2S with de-ionized water.
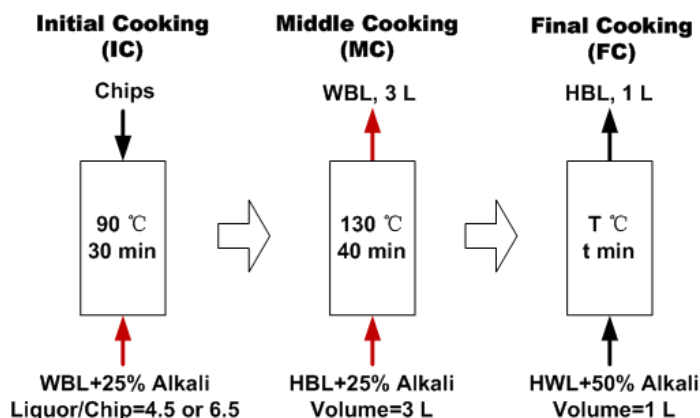

Fig. 1. Schematic flow diagram of the simulated displacement pulping process

Table 1. Pulping Conditions

Cooking No.	Alkali Charge (%)	Sulfidity (%)	Maximum T (°C)	Cooking Time (min)	Final Pulp Kappa Number
1	**18**	25	160	120	26.02
2	**20**	25	160	120	22.14
3	**23**	**15**	160	120	26.07
4	23	**20**	160	120	20
5*	23	**25**	160	120	13.05
6	23	**30**	160	120	13.68
7	23	25	**140**	120	36.96
8	23	25	**150**	120	25.9
9	23	25	**160**	120	24.56
10	23	25	**170**	**120**	18.43
11	23	25	160	**90**	21.71
12	23	25	160	**150**	14.4

* The alkali ratios at the initial, middle, and final cooking stages were 10%, 30%, and 60%, respectively.

The effective alkali (EA) charge, *i.e.*, EA = [NaOH] + 1/2 [Na_2S], was maintained at 18%, 20%, and 23% of the oven-dry feedstock. The sulfidity ([Na_2S]/([Na_2S] + [NaOH])) was maintained at 15%, 20%, 25%, and 30%. The alkali ratios used in the initial, middle, and final cooking stages were 25%, 25%, and 50%, respectively. The liquor-to-

feedstock ratio was 4.5 L/kg. The EA or sulfidity in the black liquor was adjusted by adding stock solutions of NaOH and/or Na_2S. The preset maximum cooking temperatures were 140 °C, 150 °C, 160 °C, and 170 °C. The holding times at the maximum temperature were 90 min, 120 min, and 150 min. Table 1 shows a detailed description of the experimental conditions. Figure 1 is the schematic flow diagram of the simulated displacement pulping process.

Liquor and Pulp Analysis

The cooking liquors at the lower inlet, upper outlet, and middle circulation screen of the digester were sampled, and the dissolved lignin content in the liquors was determined using the ATR-UV spectroscopic method from the literature (Aulin-Erdtman and Sanden 1968; Chai *et al.* 2003a,b).

The kappa number of the final discharged pulp was measured by the TAPPI standard method T 236 om-99 (1999).

RESULTS AND DISCUSSION

Content Profile of the Dissolved Lignin in the Cooking Liquor during the Displacement Pulping Process

Figure 2 shows the content profiles of the dissolved lignin in the cooking liquors in the three stages during displacement pulping, *i.e.*, the initial cooking stage with the WBL, the middle cooking stage with the HBL, and the final cooking stage with the HBL and HWL.
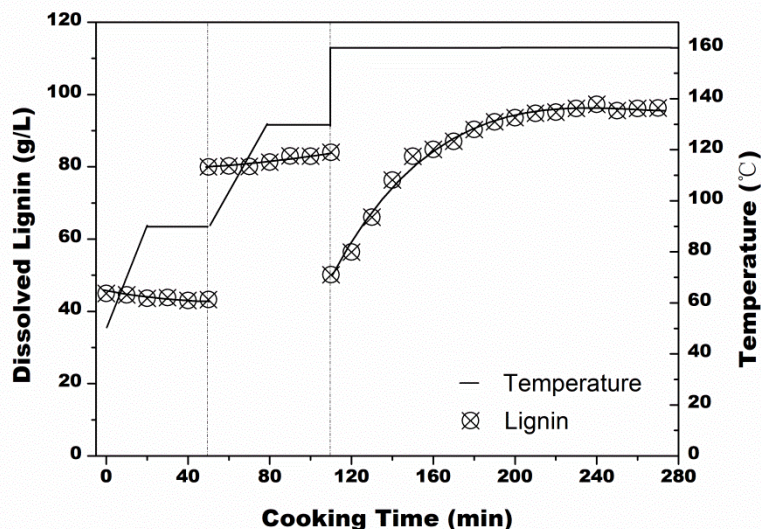

Fig. 2. Changes in the dissolved lignin content in the pulping liquor during the different cooking stages

It was found that the dissolved lignin content slightly decreased in the initial cooking stage, which was because the adjusted WBL was diluted by the moisture in the bamboo chips. The dissolved lignin content in the middle cooking stage slightly increased, which was because the temperature and EA charge were not sufficient for fast delignification. However, it was observed that major delignification took place during the

first 50 min in the final cooking stage, where the EA charge was high (39.1 g/L to 25.2 g/L) and the temperature of the cooking liquor reached 160 °C. As a result, the net increase in the lignin content in the cooking liquor was approximately 34.7 g/L. After 200 min, the increase in the dissolved lignin in the cooking liquor was not major, which meant that pulping should be terminated during this period.

Relationship between the Pulp Kappa Number and Total Dissolved Lignin in the Pulping Liquor during the Batch Process

Figure 3 shows the relationship between the pulp kappa number (measured by TAPPI Method T 236 om-99 (1999)) and integrated dissolved lignin in the pulping liquors during the batch processes with different pulping conditions (such as high or low sulfidity, with or without pulp additives, and different temperatures) measured by the ATR-UV method (Chai *et al.* 2003a). It was observed that there was an inverse relationship between the pulp kappa number and integrated dissolved lignin. It was found that the R^2 and the root mean square error (RMSE) were 0.95 and 1.07 respectively, using the inverse proportion function:

$$y = (a - x) / (b - x) + c \tag{1}$$

Therefore, the integrated dissolved lignin in the cooking liquor can be regarded as a reliable indicator of the degree of delignification during the batch pulping process.
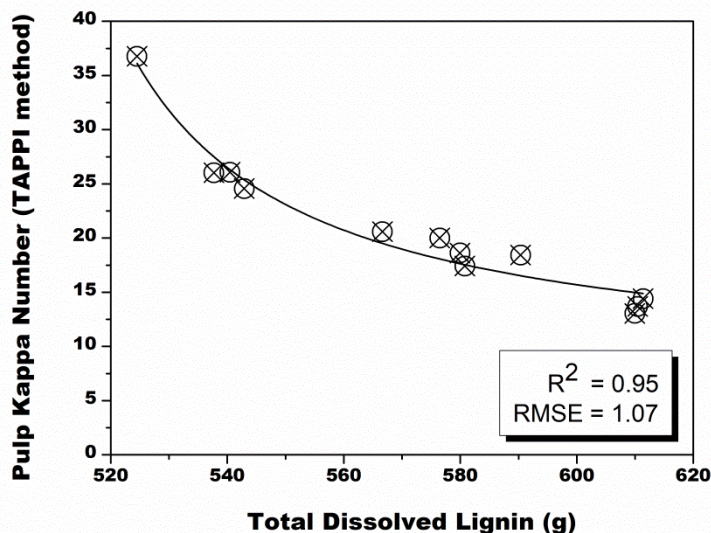

Fig. 3. Pulp kappa number *vs*. total dissolved lignin in the cooking liquor during the batch pulping process

Establishment of the Dissolved Lignin-based Model for Predicting the Pulp Kappa Number

From the fundamental laws of conservation of mass, the lignin in chips (M_i, g) is conserved during the displacement pulping process, which is divided into two parts, *i.e.*, the amount of total dissolved lignin in the pulping liquor (M_{dl}, g) and the amount of residual lignin in the pulp (M_{rl}, g) (Mattsson *et al.* 2017). The mass balance equation can be written as follows:

$$M_l = M_{rl} + M_{dl} \tag{2}$$

The chips also follow the law of conservation of mass. The mass balance equation can therefore be written as,

$$M_c = M_p + M_{cl} + M_{dl} \tag{3}$$

where M_c (g) is the weight of the chips charged to the digester, M_p (g) is the weight of the discharged pulp, and M_{cl} (g) is the amount of dissolved carbohydrates, including the dissolved hemicellulose and extractives.

It was well established that there is a good linear relationship between the pulp kappa number ($K_\#$) and instantaneous lignin content in the pulp (l),

$$K_\# = a \times l + b \tag{4}$$

where $K_\#$ is the pulp kappa number during the cooking process, and a and b are the slope and intercept of the equation, respectively (Sixta 2006).

According to Eqs. 2 and 3, the lignin instantaneous content of the pulp can be written as:

$$l = \frac{M_l - M_{dl}}{M_c - M_{cl} - M_{dl}} \tag{5}$$

In the cooking process, most of the hemicelluloses and almost all of the extractives are dissolved during the initial stage (Kondo and Sarkanen 1984; Johansson and Germgård 2008). It can be assumed that a constant amount of carbohydrates is dissolved. The amount of dissolved carbohydrates is between approximately 12% and 20% of the raw material, depending on the type of raw material and cooking conditions (Wigell *et al.* 2007; Nieminen *et al.* 2014). Therefore, the M_{cl} can be written as:

$$M_{cl} = \beta M_c, \qquad \beta \in [0.12, 0.2] \tag{6}$$

Substituting Eqs. 5 and 6 into Eq. 4 results in the following equation:

$$K_\# = a \frac{M_l - M_{dl}}{(1 - \beta)M_c - M_{dl}} + b \tag{7}$$

Therefore, the pulp kappa number during the cooking process can be calculated using Eq. 7 if the slope and intercept values in the equation are available.

The dissolved lignin concentration in the pulping liquor ($C_i(t)$) was determined using the ATR-UV sensor, and the pulping flow quantity ($Q_i(t)$) was reached with the flow meter. The total dissolved lignin in the pulping liquor at the different stages was as follows:

1) In the initial cooking stage, the total outer dissolved lignin (M_{IC}^I) is charged to the digester with the WBL:

$$M_{IC}^I = \int_{t_1}^{t_2} C_1(t)Q(t)\, dt \tag{8}$$

where t_1 and t_2 are the start and ending times of injecting the impregnation liquor into the digester, respectively.

2) In the middle cooking stage, the total outer dissolved lignin ($M_{MC}^I(t)$) is charged

to the digester with the HBL, while the total dissolved lignin ($M_{MC}^{O}(t)$) is taken out of the digester with the black liquor or WBL:

$$M_{MC}^{I}(t)=\int_{t_3}^{t}C_1(t)Q_1(t)dt \ , \ t_3 \leq t \leq t_4 \tag{9}$$

$$M_{MC}^{O}(t)=\int_{t_3}^{t}C_2(t)Q_2(t)dt \ , \ t_3 \leq t \leq t_4 \tag{10}$$

where t_3 and t_4 are the start and ending times of displacing the WBL with the HBL, respectively.

    3) In the final cooking stage, the circulation flow is only within the system. The increase in the dissolved lignin in the liquor ($M_{FC}(t)$) is remarkable when major delignification takes place:

$$M_{FC}(t)=\int_{t_5}^{t}C_3(t)Vdt \ , \ t_5 \leq t \leq t_6 \tag{11}$$

where t_5 and t_6 are the start and stop times of the heating and cooking steps, respectively, and V is the volume of the cooking liquor in the digester.

In summary, the model for the total dissolved lignin in the pulping liquor during the cooking process is as follows:

$$M_{dl}(t)=\begin{cases} M_{MC}^{O}(t)-M_{MC}^{I}(t)-M_{IC}^{I} & t_3 \leq t \leq t_4 \\ M_{FC}(t)+M_{MC}^{O}(t_4)-M_{MC}^{I}(t_4)-M_{IC}^{I} & t_5 \leq t \leq t_6 \end{cases} \tag{12}$$

Substituting Eq. 12 into Eq. 7 produces Eq. 13:

$$K_{\#}(t)=\begin{cases} a\dfrac{M_l-\left[M_{MC}^{O}(t)-M_{MC}^{I}(t)-M_{IC}^{I}\right]}{M_c-\left[M_{MC}^{O}(t)-M_{MC}^{I}(t)-M_{IC}^{I}\right]}+b & t_3 \leq t \leq t_4 \\[4mm] a\dfrac{M_l-\left[M_{FC}(t)+M_{MC}^{O}(t)-M_{MC}^{I}(t)-M_{IC}^{I}\right]}{M_c-\left[M_{FC}(t)+M_{MC}^{O}(t)-M_{MC}^{I}(t)-M_{IC}^{I}\right]}+b & t_5 \leq t \leq t_6 \end{cases} \tag{13}$$

Therefore, one can use Eq. 12 to obtain the pulp kappa number during the pulping process based on the on-line monitoring of dissolved lignin in the cooking liquor from three different stages.

Model Application

In this work, displacement kraft pulping experiments were simulated and conducted in a laboratory for which the pulping conditions, and procedures are provided in Table 1 and Fig. 1. The pulp samples (*i.e.*, the discharged pulp at the end of displacement pulping) from the different cooking processes were collected and their kappa numbers were determined by both the dissolved lignin-based model and a reference TAPPI method (T 236 om-99 1999).

Table 2 lists the pulp kappa number data obtained by both the modelling method based on measuring the dissolved lignin in the cooking liquor and the reference method based on measuring the pulp kappa number. It was found that the maximum difference

between these two test methods was within 1.98 (among 12 samples) and the maximum relative difference was 8.41%, which indicated that the present model can justifiably be used in industrial processes. Because the present model is based on measuring the dissolved lignin content in the pulping liquor, it is much easier to realize the on-line kappa number measurement than the pulp-based measurement technique.

Table 2. Method Comparisons

Cooking No.	Dissolved Lignin Content (g)	Pulp Kappa Number		Difference	Relative Difference (%)
		TAPPI Method (T236 om-99 1999)	Model Prediction		
1	537.72	26.02	25.72	0.30	1.17
2	581.40	22.14	22.90	0.76	3.45
3	540.48	26.07	28.05	**1.98**	7.59
4	576.48	20.00	19.59	0.41	2.04
5*	612.94	13.05	13.72	0.67	5.17
6	610.44	13.68	13.30	0.38	2.80
7	520.52	36.96	35.84	1.12	3.04
8	564.04	25.90	24.66	1.24	4.77
9	562.92	24.56	25.52	0.96	3.89
10	600.36	18.43	19.98	1.55	**8.41**
11	592.06	21.71	20.38	1.33	6.13
12	609.96	14.40	13.72	0.68	4.69

CONCLUSIONS

1. Based on the fundamental principles of mass during displacement pulping and the ATR-UV spectroscopic technique, a novel mathematical model for end-point control was explored during the displacement kraft pulping process.

2. After the theoretical analysis, it was found that there was an inverse relationship between the pulp kappa number and integrated dissolved lignin content. Therefore, the model was developed by monitoring the changes in the dissolved lignin content in the cooking liquor using the ATR-UV spectroscopic technique.

3. The results showed that there was a good relationship between the pulp kappa numbers measured by the presented model and TAPPI standard method (T 236 om-99 1999).

4. This new method is straightforward and practical, and it can become a valuable tool for the on-line monitoring of the pulp kappa number during the displacement batch pulping process.

ACKNOWLEDGMENTS

REFERENCES CITED

Aulin-Erdtman, G., and Sanden, R. (1968). "Spectrographic contributions to lignin chemistry," *Acta Chem. Scand.* 22, 1187-1209.

Brown, R. (2014). "Agenda 2020: Next generation chemical pulping," *Tappi J.* 13(10), 10-11.

Chai, X. S., Hou, Q. X., Zhu, J. Y., and Ban, W. (2003a). "Online monitoring of alkali, sulfide, and dissolved lignin during wood pulping by attenuated total reflection-ultraviolet spectroscopy and flow injection techniques," *Ind. Eng. Chem. Res.* 42(2), 254-258. DOI: 10.1021/ie0204585

Chai, X. S., Luo, Q., and Zhu, J. Y. (2000). "A simple and practical pulp kappa test method for process control in pulp production," *Process Contr. Qual.* 11(5), 407-417. DOI: 10.1163/156856600750250798

Chai, X. S., Zhu, J. Y., Luo, Q., and Li, J. (2003b). "Attenuated total reflection UV spectroscopy for simultaneous analysis of alkali, sulphide and dissolved lignin in pulping liquors," *J. Pulp Pap. Sci.* 29(6), 204-207.

Chari, N. C. S. (1973). "Integrated control system approach for batch digester control," *Tappi J.* 56(7), 65-68.

Christensen, T. (1982). *A Mathematical Model of the Kraft Pulping Process*, Ph.D. Thesis, Purdue University, West Lafayette, IN.

Faix, O., Welkener, U., and Patt, R. (1988). "Method for controlling the digestion of pulp by IR spectroscopy," U. S. Patent No. 4743339A.

Gustafson, R. R., Sleicher, C. A., McKean, W. T., and Finlayson, B. A. (1983). "Theoretical model of the kraft pulping process," *Ind. Eng. Chem. Proc. DD* 22(1), 87-96. DOI: 10.1021/i200020a016

Hatton, J. V. (1973). "Application of empirical equations to process control," *Tappi J.* 56(8), 108-111.

Johansson, D., and Germgård, U. (2008). "Carbohydrate degradation during softwood kraft cooking - Influence on cellulose viscosity, carbohydrate composition and hexenuronic acid content," *Nord. Pulp Pap. Res. J.* 23(3), 292-298. DOI: 10.3183/NPPRJ-2008-23-03-p292-298

Kesavan, P., Lee, J. H., Saucedo, V., and Krishnagopalan, G. A. (2000). "Partial least squares (PLS) based monitoring and control of batch digesters," *J. Process Contr.* 10(2-3), 229-236. DOI: 10.1016/S0959-1524(99)00028-1

Kerr, A. J. (1976). "The kinetics of kraft pulping - Batch digester control," *Tappi J.* 59(5), 89-91.

Kondo, R., and Sarkanen, K. V. (1984). "Kinetics of lignin and hemicellulose dissolution during the initial stage of alkaline pulping," *Holzforschung* 38(1), 31-36. DOI: 10.1515/hfsg.1984.38.1.31

Lee, Q. F., and Bennington, C. P. J. (2007). "Spat a distribution of kappa number in batch digesters: 2D model," *J. Pulp Pap. Sci.* 33(4) C27-C38.

Masura, V. (1999). "A mathematical model of kraft pulping related to the alkali concentration in the cooking liquor," *Wood Sci. Technol.* 33(5), 381-389. DOI: 10.1007/s002260050124

Mattsson, C., Hasani, M., Dang, B., Mayzel, M., and Theliander, H. (2017). "About structural changes of lignin during kraft cooking and the kinetics of delignification," *Holzforschung* 71(7-8), 545-553. DOI: 10.1515/hf-2016-0190

Michell, A. J. (1990). "Kappa number determination in kraft pulping by NIR spectroscopic measurements on spent liquors," *Tappi J.* 73, 235-236.

Nieminen, K., Paananen, M., and Sixta, H. (2014). "Kinetic model for carbohydrate degradation and dissolution during kraft pulping," *Ind. Eng. Chem. Res.* 53(28), 11292-11302. DOI: 10.1021/ie501359p

Pelzer, R., Dörrer, H., Hemmes, J.-L., Moormann-Schmitz, A., Höötmann, U., Blickenstorfer, C., Kramer, G., Otto, K., Hörsken, A., Opalka, A., *et al*. (2013). "Process chemicals," in: *Handbook of Paper and Board*, H. Holik (ed.), Wiley-VCH Verlag, Weinheim, Germany, pp. 291-349.

Santos, R. B., Gomide, J. L., and Hart, P. W. (2015). "Kraft pulping of reduced metal content eucalyptus wood: Process impacts," *BioResources* 10(4), 6538-6547. DOI: 10.15376/biores.10.4.6538-6547

Saucedo, V. M., and Krishnagopalan, G. A. (2000). "Application of *in-situ* near infrared analysis for the measurement of cooking liquor components during kraft pulping," *J. Pulp Pap. Sci.* 26, 25-30.

Sixta, H. (2006). *Handbook of Pulp*, Wiley-VCH Verlag, Weinheim, Germany.

T 236 om-99 (1999). "Kappa number of pulp," TAPPI Press, Atlanta, GA.

Tasman, J. E. (1981). "Kraft delignification models," *Tappi J.* 64(3), 175-176.

Trung, T. P., Betts, S. P. A., and LeClerc, D. F. (2009). "Method for determining chemical pulp kappa number with visible-near infrared spectrometry," U. S. Patent No. 7604712B2.

Vanchinathan, S., and Krishnagopalan, G. A. (1995). "Kraft delignification kinetics based on liquor analysis," *Tappi J.* 78(3), 127-132.

Venkateswarlu, C., and Gangiah, K. (1992). "Dynamic modeling and optimal state estimation using extended Kalman filter for a kraft pulping digester," *Ind. Eng. Chem. Res.* 31(3), 848-855. DOI: 10.1021/ie00003a029

Vroom, K. E. (1957). "The H factor: A means of expressing cooking times and temperatures as a single variable," *Pulp Paper Mag. Can.* 58(3), 228-231.

Wigell, A., Brelid, H., and Theliander, H. (2007). "Degradation/dissolution of softwood hemicellulose during alkaline cooking at different temperatures and alkali concentrations," *Nord. Pulp Pap. Res. J.* 22(4), 488-494. DOI: 10.3183/NPPRJ-2007-22-04-p488-494