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Research Article

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Kinetics research of wheat straw sodium sulfate-AQ pulping process

Wei Song[1] and Jianming Liu[2]

[1]*Tianjin Key Laboratory for Control Theory & Applications in Complicated Systems, Tianjin University of Technology, Tianjin, China*
[2]*College of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin, China*

ABSTRACT

This paper researched into the delignification mechanism and the relations of black liquor lignin content and alkali concentration to pulping time under the cooking process conditions of wheat straw sodium sulfate-anthraquinone(AQ) pulping with Microwave radiation. The results showed that delignification process was divided into two stages: quick stage and slow stage. The lignin removal rate in the first stage was much higher than the second stage, that is, lignin has been removed more sufficiently after quick stage. In this stage, reaction order of delignification was 1.5, and 0.5 with respect to OH^-, the activation energy was 51.90 kJ • mol^{-1}. The latter delignification belonged to the first-order reaction and 0.3 with respect to OH^-, the activation energy was 72.20 kJ • mol^{-1}KJ. Apparently, slow stage needed to consume large amounts of energy to removal lignin.

Key words: lignin; pulping; delignification; kinetics; reaction order

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INTRODUCTION

Chinese pulp is mainly non-wood, that is, straw pulping. Each year straw pulp production accounts for about 80% of the worlds', and wheat straw pulp is widely used. With the rise of the pulp industry, a variety of pulping process matures. The traditional pulping process, such as sodium sulfate - AQ method, has the advantages of high yield, low hardness and good whiteness [1]. The reaction mechanism and kinetics processes have been explored [2, 3]. But generally the traditional pulping process is energy-intensive, time-consuming, and is kind of contrary to the theme of "energy saving" in today's economic development. Microwave is a high-frequency electromagnetic wave, accompanied by high-energy electromagnetic fields. In the electromagnetic field, the materials absorb microwave energy to produce a high heat [4]. Compared with the traditional process, the adoption of appropriate cooking can greatly facilitate the diffusion speed of the cooking liquid in the raw materials, accelerate the chemical reaction and the dissolution of the lignin, shorten the cooking time, increase production efficiency, and reduce the consumption of energy in the conditions of the atmospheric environment and the microwave radiation[5,6]. Kinetics research of wheat straw microwave radiation pulping process can not only describe the dissolving law of some components in microwave cooking process and can be used as the theoretical basis for optimization of existing pulping process. This paper researched into the delignification mechanism and the relations of black liquor lignin content and alkali concentration to pulping time in cooking process. The reaction kinetics equations of wheat straw sodium sulfate-AQ Pulping with Microwave radiation were established.

EXPERIMENTAL SECTION

2.1The Experimental Materials, Chemicals and Instruments

Wheat straw (from pulp and paper laboratory of Tianjin University of Science and Technology); Anthraquinone(AQ), chemically pure(from Shanghai Chemical Reagent Factory); sodium sulfate, chemically pure (from Tianjin Guangfu Fine Chemical Research Institute); sodium hydroxide AR, hydrochloric acid (36% -38%), sodium sulfide, 95% ethanol and anhydrous ethanol, acetic acid, benzene, acetone, etc. (from Tianjin chemical

Reagent wholesale company).

Microwave Digestion System (EIHOS A), Shanghai Xinyi Microwave Chemical Technology Co., Ltd.; UV - visible spectrophotometer (Cary 50), Shanghai Kuiyuan Scientific Instruments Co., Ltd.; Fluorescence microscopy (ECLIPSE Ti-u models), Beijing Ruike Instrument Technology Co., Ltd.; the pH meter (Delta 320), Jiangsu province Wuxi zhongheng experiment instrument Co., LTD.

2.2 Pretreatment of Raw Material

The ear, skin, and the junction of wheat straw were removed, and cut into 2-3 cm in order to guarantee the stability and unity of the composition during the experiment. Its chemical composition is[7,8]: moisture 6.57%, lignin 15.90%, the cold water extract 10.36%, the hot water extract 18.20% , 1% NaOH extract 46.13%, benzene-alcohol extract 1.99%, holocellulose 71.37%, cellulose 38.76%.

2.3 Kinetics Experiments of Microwave Radiation Wheat Straw Sulfate - AQ Pulping

Microwave radiation pulping was conducted on the basis of traditional sulfate - AQ pulping process [9]. Microwave digestion instrument power was 450 W. The experimental conditions: temperature 110 -140 ℃, alkali content 7%, Na2S 1%, the AQ 0.025%, liquor ratio of 1:20. Measure the black liquor pH and diluted 100-fold black liquor lignin absorbance each time, and calculate the lignin content using the linear relationship between lignin concentration and absorbance.

RESULTS AND DISCUSSION

3.1 Analysis of Cooking Process

The amount of delignification was gradually increasing and alkali was consumed with the extension of the cooking time during cooking process. Here removal lignin process was analyzed at 120 ℃. It was delignification situation of initial state and cooking for 90 min. It can be observed that wheat straw cell structure ruptured, lignin dissolved and removed for cooking 90 min under a fluorescence microscope (Figure 1). The photos showed the remaining slender cellulose. It could be obtained that process of pulp cooking basically completed by breaking apart process.

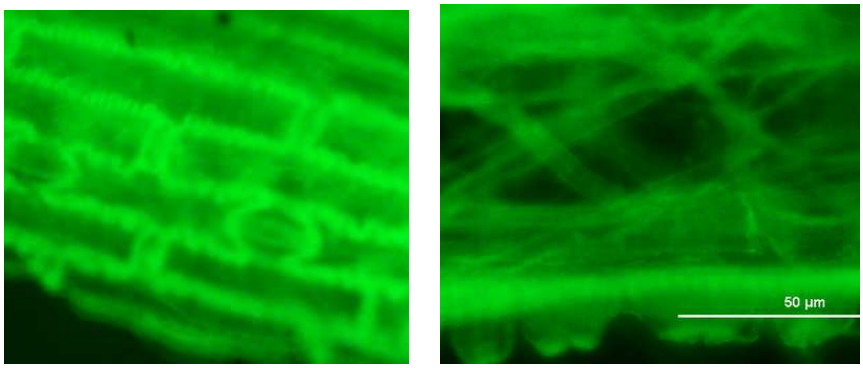

Figure 1 Wheat straw fiber structure of initial state and cooking for 90 min

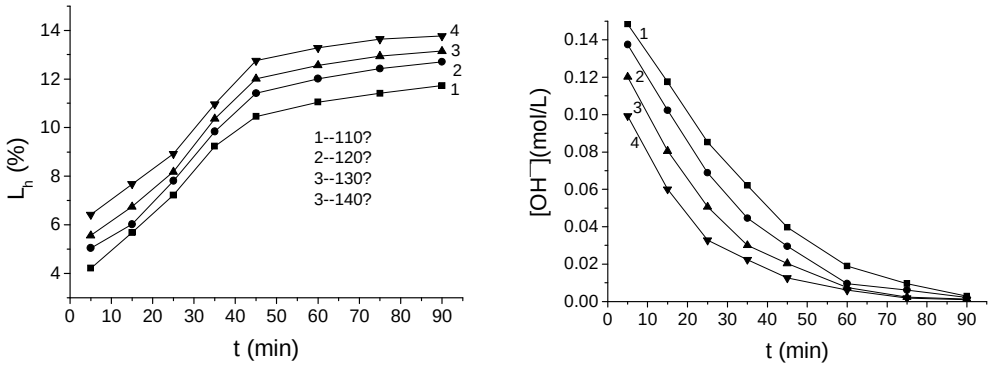

Figure2 Changes of lignin content L_h and alkali concentration [OH^-] with cooking time

3.2 Analysis of Black Liquor Lignin Content and Alkali Concentration in Cooking Process

The lignin removed was left in the black liquor in pulping process. The higher the lignin content was in the black

liquor, the greater rate of removal lignin in the pulp. In the appropriate cooking process conditions, black liquor pH value was determined, and alkali concentration[OH-] and the lignin content Lh were calculated at different temperature and time. The changes of lignin content and alkali concentration with cooking time were shown in Figure 2.

Figure 2 displayed the process of delignification in the cooking process. It can be clearly divided into two phases: quick delignification stage and slow delignification stage. When the cooking time was close to 45min, lignin had been more fully removed and the average removal lignin rate was 73.1%. For 45-90min slow lignin removal stage, the removal rate gradually increased to 84.6%. The rate of lignin removal rose slowly. That might be that the longer the cooking time can result in lignin polymerization or suck back in pulping conditions of microwave radiation.

3.3 Analysis of delignification reaction kinetics in cooking process

3.3.1 Determination of reaction order, reaction rate constant

Under the conditions of the cooking process, the changes of black liquor lignin content and alkali concentration with the cooking time in the different experimental temperature were shown in Table 1.

Table 1 Measured Results of Lignin Content and [OH^-] at Different Temperatures

T(℃)	Time (min)	quick stage				slow stage			
		5	15	25	35	45	60	75	90
110	Lignin Content L_h(%)	4.21	5.68	7.22	9.23	10.46	11.05	11.41	11.73
	$[OH^-]\times10^3$ (kmol/L)	0.1484	0.1175	0.0852	0.0621	0.0396	0.0190	0.0096	0.0028
120	Lignin Content L_h(%)	5.05	6.02	7.81	9.84	11.41	12.01	12.42	12.71
	$[OH^-]\times10^3$ (kmol/L)	0.1375	0.1023	0.0689	0.0464	0.0295	0.0096	0.0060	0.0020
130	Lignin Content L_h(%)	5.56	6.75	8.18	10.36	12.01	12.56	12.94	13.15
	$[OH^-]\times10^3$ (kmol/L)	0.1202	0.0805	0.0506	0.0300	0.0204	0.0075	0.0023	0.0013
140	Lignin Content L_h(%)	6.12	7.68	8.92	10.96	12.76	13.28	13.64	13.77
	$[OH^-]\times10^3$ (kmol/L)	0.0993	0.0601	0.0327	0.0224	0.0125	0.0060	0.0017	0.0010

The lignin removed was left in the black liquor in pulping process. The higher the lignin content was in the black liquor, the greater rate of removal lignin in the pulp. In the cooking process, the delignification reaction rate was expressed as: $-\frac{dL}{dt}=\frac{dL_h}{dt}=kL^n[OH^-]^m$ (1)

Equation (1): L- pulp lignin content at a certain time(%); Lh - black liquor lignin content at a certain time (%); [OH-] - alkali concentration at a certain time (kmol / L); t-cooking time(min); k-delignification reaction speed constant; n&m- reaction orders for L and [OH-].

Take the logarithm for equation (1):

$$\lg\frac{dL_h}{dt}=\lg k+n\lg L+m\lg[OH^-] \quad (2)$$

Write equation (2) as the differential:

$$\lg\frac{\Delta L_h}{\Delta t}=\lg k+n\lg L+m\lg[OH^-] \quad (3)$$

Processing the measured data in Table 1 using the least squares method for the binary linear regression equation [10], reaction rate constants and reaction orders can be obtained. The fitting results were shown in Table 2.

Table2 Fitting results of kinetics in cooking processes

T (℃)	quick stage			slow stage		
	reaction orders		k×10^3	reaction orders		k×10^3
	n	m	$[L\cdot kmol^{-1}]^m\cdot min^{-1}$	n	m	$[L\cdot kmol^{-1}]^m\cdot min^{-1}$
110	1.4915	0.5158	0.8016	1.0290	0.2696	0.1104
120	1.4997	0.5271	0.5911	1.0397	0.3190	0.0592
130	1.5084	0.5372	0.4022	1.0598	0.3219	0.0328
140	1.5430	0.5494	0.2452	1.1047	0.3259	0.0212

The fitting results showed that reaction order of delignification was 1.5, and 0.5 with respect to OH^- in the first stage, and the latter delignification belonged to the first-order reaction and 0.3 with respect to OH^-.

3.3.2 Determination of the activation energy

Reaction rate constant varies with temperature. The relation between them should satisfy the formula of the Arrhenius:

$$k = Ae^{\frac{-Ea}{RT}}$$

Ea-activation energy (J/ mol); A-exponential factor, the same units as k; the R- gas constant, 8.314J / (mol • K).

Table 3 The reaction rate constant of different temperatures at the different stages

$1/T\times10^3$ (1/K)	quick stage				slow stage			
	$k\times10^3$	Ln k	Ea (kJ/mol)	A	$k\times10^3$	Ln k	Ea (kJ/mol)	A
2.4213	0.8016	-7.1289	51.90	3.05×10^3	0.1104	-9.1114	72.70	1.62×10^5
2.4814	0.5911	-7.4335			0.0592	-9.7346		
2.5445	0.4022	-7.8186			0.0328	-10.3251		
2.6110	0.2452	-8.3134			0.0212	-10.7615		

The curves of *lnk* versus *1/T* were plotted and fitted linearly in Figure 3. The apparent activation energies and exponential factors at quick stage (line 1) and slow stage (line 2) can be obtained. The results were shown in table 3. The activation energy of quick delignification stage was less than the slow one. This may be explained that small molecular weight lignin was dissolved mainly at quick delignification stage. The high molecular weight lignin was gradually stripping, which need more energy to destroy the chemical bonds between the macromolecular lignin.

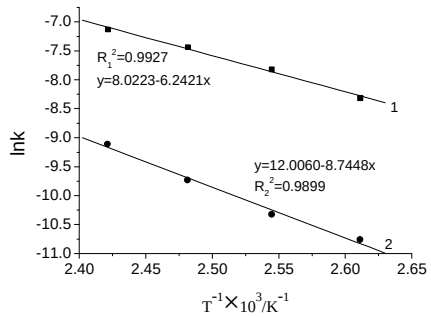

Figure 3 The relation plot of rate constant and temperature

Kinetics equations of wheat straw sodium sulfate-AQ pulping with microwave radiation can be summarized by the calculation of reaction orders and activation energies as follows.

Quick delignification stage：

$$-\frac{dL}{dt} = kL^n[OH^-]^m = Ae^{\frac{-Ea}{RT}}L^n[OH^-]^m = 3.05\times10^3\exp\left(\frac{-51900}{RT}\right)L^{1.5}[OH^-]^{0.5}$$

Slow delignification stage：

$$-\frac{dL}{dt} = kL^n[OH^-]^m = Ae^{\frac{-Ea}{RT}}L^n[OH^-]^m = 1.62\times10^5\exp\left(\frac{-72700}{RT}\right)\mathrm{L}[OH^-]^{0.3}$$

CONCLUSION

1. The delignification mechanism and the relations of black liquor lignin content and alkali concentration to pulping time were studied under the cooking process conditions of wheat straw sodium sulfate-AQ pulping with Microwave radiation. The results showed that delignification process was divided into two stages: quick delignification stage and slow delignification stage. These two delignification stages were to follow certain rules of reaction kinetics.

2. The rules of reaction kinetics were obtained. The lignin removal rate in quick stage was much higher than slow stage, that is, lignin has been removed more sufficiently after quick stage. In the first stage, reaction order of delignification was 1.5, and 0.5 with respect to OH-, the latter delignification belonged to the first-order reaction and 0.3 with respect to OH-.

3. In microwave radiation straw sulfate – AQ pulping process, the apparent activation energies of quick delignification stage and slow one were 51.90 and 72.20KJ/mol respectively. Apparently, the later needed to consume larger than the former.

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REFERENCES

[1] Long Zhu; Xu Yongying; Li Zhiqing. *Transactions of China Pulp and Paper.* **1997**, (12), 10-17.
[2] Huang Guolin; Zhou Lixia; Chen Zhongsheng. *Journal of East China University of Science and Technology*. **2003**,29(3), 234-238.
[3] Sun Yong; Zhang Jinping; Yang Gang; Li Zuohu. *Journal of Cellulose Science and Technology*. **2007**, 15(3), 14-19.
[4] Zhang Jianwei; Deng Yu. *Heilongjiang Paper*. **2008**, (3), 18~23.
[5] Ooi B. G. ; Rambo A. L. ; Hurtado M. A. *Journal of Molecular Science*. **2011**, 12(3), 1451-1463.
[6] Chen Yihui; Li Hui; Lin Hetong. ICAE 2011. **2011**, 793-796.
[7] Liu Shucha. Analysis and testing of pulp and paper. Chemical Industry Press, Beijing. **2003**, 13-21.
[8] Yang Q, Wu SB. *Cellulose Chemistry and Technology*. 2**0**09, (43), 133-139.
[9] Qin Menghua, Fu Yingjuan, Wang Zhen, Liu Nali. *Transactions of China Pulp and Paper*. **1998**, (13), 16-21.
[10] Obrocea PP; Teodorescu GN. *Cellulose Chemistry and Technology*. **2005**, (29), 247-252.