

Pulping of Wheat Straw with Caustic Potash-Ammonia Aqueous Solutions and Its Kinetics^{*}

HUANG Guolin(黄国林)^{a,**}, ZHANG Chengfang(张成芳)^b and CHEN Zhongsheng(陈中胜)^a

^a Department of Chemical Engineering, East China Institute of Technology, Jiangxi 344000, China

^b Institute of Chemical Technology, East China University of Science and Technology, Shanghai 200237, China

Abstract A pulping technology of wheat straw with aqueous ammonia and diluent caustic potash was investigated. Because its strong alkalinity, the addition of caustic potash not only reduced the quantity of NH_3 consumed and cooking time, but also enriched the black liquor with nutrients such as potassium and nitrogen, which could be used as fertilizer for agriculture. Various pulping conditions including composition of cooking liquor, liquor-to-solid ratio, maximum cooking temperature, time to reach the maximum temperature and time at the maximum temperature were studied systematically to determine the suitable pulping conditions. Results of the cooking course showed that there were three distinct delignification phases, namely, the bulk delignification phase from the beginning of cooking to 100°C, the supplementary delignification phase from 100°C to 155°C for 45min and the third delignification phase till the end of cooking. The rate of delignification was found to be first order with respect to residual lignin and 0.34 order with respect to $[\text{OH}^-]$. The activation energy of the delignification reaction was $29.75\text{kJ}\cdot\text{mol}^{-1}$ and the rate equation of delignification was also obtained.

Keywords pulping, wheat straw, kinetics, delignification

1 INTRODUCTION

Under the pressure of rising consumption on wood resource, more attention has been paid to using non-wood raw materials in papermaking industry. Pulping on non-wood fiber material is expected to increase from 7%—8% at the present to 10%—15% in 2010 in the world^[1]. Non-wood material, particularly wheat straw, are exploited as the main raw material for papermaking in China because of the limited wood resource with a forest coverage of only 13.94%^[2]. The main problem that hinders the intensive use of non-wood raw materials in papermaking industry is the environmental pollution caused by black liquor^[3].

An effective method to solve the pollution problem of black liquor is to develop new pulping technologies^[4–6]. Huang *et al.*^[7] have reviewed the improved technologies of pulping non-wood materials. In the review, aqueous ammonia was used to pulp non-wood materials for controlling pollution of black liquor, by using the black liquor which contains nutrition elements of nitrogen, potassium and some organic substances as fertilizers. But no application with aqueous ammonia for pulping appeared feasible because it needs high concentration of ammonia and prolonged cooking time for pulping. Recently, Kenji *et al.*^[8] reported some preliminary results of pulping rice straw with liquor $\text{NH}_4\text{OH-KOH}$. The details of the results, however, have not been published yet.

In this article, a pulping method of wheat straw with aqueous ammonia containing a small amount of caustic potash (KOH) as the cooking liquor and the

kinetics of delignification are reported. The black liquor is no longer a pollutant, instead it can be utilized as fertilizer for agriculture, which is of great significance for papermaking industry, environmental pollution control and agriculture.

2 MATERIALS AND PULPING CONDITION

2.1 Materials

Wheat straw harvested from the suburban of Shanghai city, China was used as the raw material. Their chemical composition is listed in Table 1.

Table 1 Chemical composition of wheat straw batch used in this study

Composition, % (by mass)	
moisture	9.08
SiO_2	4.59
lignin	26.43
pentosan	22.50
cellulose	34.33

Note: The detailed testing methods of all indexes are from Ref.[9].

2.2 Pulping Conditions

A 0.5L stainless steel digester with a stirrer and a temperature controller was used. 25.0g of the wheat straw sample, 2—3cm long in length, were presoaked in cooking liquor for 2h, and then fed into the digester. The temperature of cooking was increased from room temperature to the preset value and then kept constant for a given period of time. After cooking, the black

Received 2005-10-08, accepted 2006-04-12.

^{*} Supported by the Natural Science Foundation of Jiangxi Province (No.0520003).

^{**} To whom correspondence should be addressed. E-mail: guolinhuang@sina.com

liquor was separated from the pulp by filtration and the pulp was washed thoroughly with water. Then pulp and black liquor were analyzed separately.

Various pulping conditions including composition of cooking liquor (mass of KOH per mass of oven-dry-wheat straw, C_1 , $\text{g}\cdot\text{g}^{-1}$; mass of NH_3 per mass of oven-dry-wheat straw, C_2 , $\text{g}\cdot\text{g}^{-1}$), the ratio of liquor-to-solid (volume of cooking liquid per mass of oven-dry-wheat straw, R_{LS} , $\text{ml}\cdot\text{g}^{-1}$), the maximum cooking temperature (T_{max} , $^{\circ}\text{C}$), time to reach maximum temperature (t_1 , min) and the time at maximum temperature (t_2 , min), which affect degree of delignification and pulp yield were studied systematically by experiments. The optimal pulping condition is summarized in Table 2. Further details about it can be found in a previous work^[10].

Table 2 Suitable technological conditions of pulping of wheat straw

C_1 , $\text{g}\cdot\text{g}^{-1}$	C_2 , $\text{g}\cdot\text{g}^{-1}$	R_{LS} , $\text{ml}\cdot\text{g}^{-1}$	T_{max} , $^{\circ}\text{C}$	t_1 , min	t_2 , min
5	25	8:1	155	60	45

3 RESULTS AND DISCUSSION

3.1 Pulping course

Pulping experiments were carried out under the optimal conditions shown in Table 2 except pulping time lasted to 210min. Pulp obtained at different pulping time was washed, dried and crushed, then the contents of lignin and SiO_2 were measured. Effective alkali of black liquor was measured with potentiometric titration. BaCl_2 was added for precipitating lignin before titration and pH of 5.10 was the titration ending point. The change of chemical components with pulping time is shown in Fig.1. The relationship of cooking temperature with pulping time is marked in Fig.1(a).

3.2 Concentration change of lignin and silicon dioxide during cooking

As illustrated in Fig.1(a), delignification process could be divided into three phases. The first one is a bulk delignification phase from the beginning of cooking to 100°C . 64.70% of lignin was easily removed during this phase due to the structure of lignin unit and chemical property of wheat straw^[11]. The second one is the supplementary delignification phase from 100°C to 155°C in 45min. In the supplementary phase, 20.99% of lignin was removed and the degree of delignification reached 85.69%, in which the raw material was turned into the pulp. The third one is the residual phase till the end of the cooking. The degree of delignification increased only a little from 85.69% to 91.63% while the degree of degradation of carbohydrate increased and the pulp yield decreased from 48.30% to 40.17%, which was not favorable to cooking quality.

It can be observed in Fig.1(a) that the silica re-

moval is up to 77.33% during the first phase of cooking to 100°C . The silica removal could be explained as the dissolution process of silica in the alkaline solution and it is easier than the delignification. In the second phase from 100°C to the end of cook, only 9.37% more of silica was removed. It was verified by experiments that removal of silica was helpful to delignification^[12].

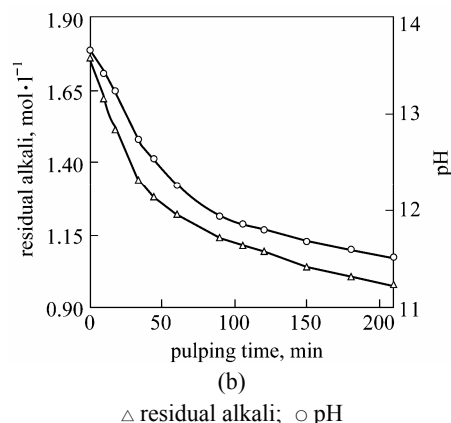
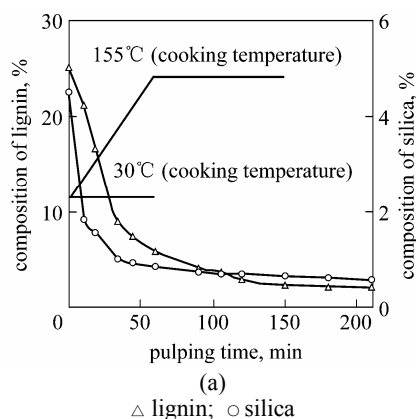


Figure 1 Changes of chemical compositions with pulping time during this pulping process

3.3 Changes of effective alkali(EA) concentration and pH in the cooking

Cooking liquor in this pulping process is a mixture of strong alkali and weak alkali, therefore, the changes of EA and pH have their own characteristics and are different from that in conventional alkaline pulping. It is shown in Fig.1(b) that pH decreased from 13.67 to 12.85 and EA from $1.78\text{mol}\cdot\text{L}^{-1}$ to $1.34\text{mol}\cdot\text{L}^{-1}$ respectively in the bulk delignification phase. KOH is strong alkali, it ionizes completely while the ionization of NH_4OH depends on the thermodynamic equilibrium. At the end of the bulk delignification phase, pH was lowered to 12.85, suggesting that there was some unreacted KOH in the cooking liquor. In the supplementary delignification phase, pH varied from 12.85 to 11.95 while EA decreased from $1.34\text{mol}\cdot\text{L}^{-1}$ to $1.11\text{mol}\cdot\text{L}^{-1}$. It also indicated some OH^- ions from KOH still existed in the solution. In the residual phase, pH varied from 11.95 to 11.53 and

EA from $1.11\text{mol}\cdot\text{L}^{-1}$ to $0.98\text{mol}\cdot\text{L}^{-1}$ respectively, indicating that the KOH was consumed completely at the end of the cooking. During this residual delignification phase, carbohydrate is degraded seriously, requiring that the time at the maximum temperature should not be beyond 45min.

3.4 Characteristics of the pulping using KOH-NH₄OH solution

Aqueous ammonia is known as a weak alkali. When it is used as a cooking agent alone, the pulping process is uneconomic and impractical because a large quantity of ammonia (0.53g per g of straw) needs to be used with an extended period of cooking time (3h). It is discovered in our experiment that with addition of small amount of KOH, not only can the quantity of ammonia be reduced to $0.25\text{g}\cdot\text{g}^{-1}$, but also the cooking time is dramatically reduced to about 2h. The results indicate that KOH accelerates the delignification process.

It is generally known that alkaline pulping of wood has to be carried out at higher temperature (165—175°C). Wheat straw, compared with wood, can be pulped more easily at lower temperature (155°C) due to the structure of lignin unit and special chemical property. In fact, it has been reported that bulk phase of delignification of wheat straw occurs before 100°C with 50%—70% removal of total lignin^[13,14]. Thus, cooking in aqueous ammonia under lower temperature does not lead to much cellulose depolymerization and may decrease the amount of dissolved hemicelluloses, resulting in higher pulp yield, as shown in our experiments.

The physical and chemical indexes of black liquor and pulp of this pulping process are listed in Table 3.

Table 3 Physical and chemical indexes of black liquor and pulp evaluation

Indexes	Measured value
physical and chemical index of black liquor	
pH	9.63
solid matters, $\text{g}\cdot\text{L}^{-1}$	104.7
SiO_2 , $\text{g}\cdot\text{L}^{-1}$	2.46
lignin, $\text{g}\cdot\text{L}^{-1}$	30.5
suspend substance(SS), $\text{mg}\cdot\text{L}^{-1}$	1026
chemical oxygen demand (COD _{cr}), $\text{mg}\cdot\text{L}^{-1}$	73528
biological oxygen demand (BOD ₅), $\text{mg}\cdot\text{L}^{-1}$	9391
total nitrogen, $\text{g}\cdot\text{L}^{-1}$	4.26
total potassium, $\text{g}\cdot\text{L}^{-1}$	6.65
pulp evaluation	
apparent density, $\text{g}\cdot\text{m}^{-3}$	0.53
tensile index, $\text{N}\cdot\text{m}^2\cdot\text{g}^{-1}$	43.2
tear index, $\text{mN}\cdot\text{m}^2\cdot\text{g}^{-1}$	5.25
burst index, $\text{kPa}\cdot\text{m}^2\cdot\text{g}^{-1}$	1.32

For this pulping procedure, many organic compounds of wheat straw are dissolved into the cooking liquor to form ammoniacal black liquor. This black liquor contains nitrogen and potassium and inorganic substances, which can be applied as fertilizer. This application is of great significance for environmental protection because the pollution issue of black liquor can be alleviated.

4 KINETICS OF DELIGNIFICATION

There was some research on kinetics of delignification on non-wood material such as reed, wheat straw, rice straw, bagasse, agrimony, mulibamboo^[15–21]. In NH₄OH-KOH pulping of wheat straw, cooking liquor is the mixture of strong alkali with weak alkali, pH is subjected to larger change than the conventional alkaline pulping during cook process, so the knowledge on the kinetics must be different from the above mentioned. Kinetic experiments took place under the following conditions: the contents of KOH and NH₃ were held at 0.05g per g of straw and $0.25\text{g}\cdot\text{g}^{-1}$ respectively, while the liquid-to-solid ratio was 8:1. The pulp and black liquor were obtained at certain time under given pulping temperature, and then the content of lignin and pH of black liquor were measured, and are listed in Table 4.

Delignification rate in the cooking can be expressed by

$$-\frac{dL}{dt} = kL^n[\text{OH}^-]^m \quad (1)$$

and it is turned into the logarithmic form:

$$\ln\left(-\frac{dL}{dt}\right) = \ln k + n \ln L + m \ln[\text{OH}^-] \quad (2)$$

In the form of differential equation, it becomes:

$$\ln\left(-\frac{\Delta L}{\Delta t}\right) = \ln k + n \ln L + m \ln[\text{OH}^-] \quad (3)$$

Experimental data in Table 4 were handled in multi-variable linear regression by the least square method and the results are listed in Table 5.

It is seen in Table 5, the order of reaction ranged from 0.8477 to 1.089 with respect to residual lignin and from 0.2823 to 0.4006 with respect to $[\text{OH}^-]$ respectively. It is concluded that the delignification is first order with respect to residual lignin and 0.34 order with respect to $[\text{OH}^-]$. An Arrhenius equation is applicable for the rate constant:

$$\ln k = \ln k_0 - \frac{E}{RT} \quad (4)$$

A plot of $\ln k$ vs T^{-1} has been shown in Fig.2 and the correlation coefficient of the straight line is 0.9947 with the activation energy corresponds to $29.75\text{kJ}\cdot\text{mol}^{-1}$. Then the kinetics equation is

$$-\frac{dL}{dt} = 7.602 \times 10^2 \exp\left(-\frac{3577}{T}\right) L[\text{OH}^-]^{0.34} \quad (5)$$

Results of delignification rate calculated by

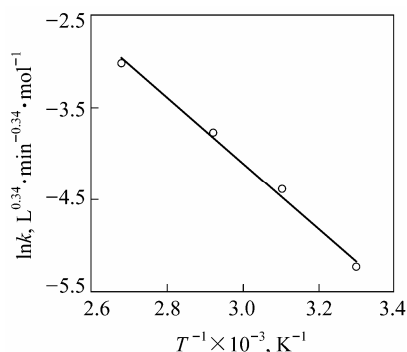
Table 4 Measured results of remaining lignin and pH at different temperatures

T	t	L_t	pH	$[\text{OH}^-]_t$	L	$\ln L$	$\ln(-dL/dt)$	$[\text{OH}^-]$	$\ln[\text{OH}^-]$
30	30	25.30	13.50	0.316					
	60	24.25	13.48	0.304	24.78	3.210	-2.850	0.310	-1.170
	90	22.90	13.44	0.280	23.58	3.170	-2.900	0.292	-1.230
	120	21.38	13.42	0.264	22.14	3.100	-2.980	0.272	-1.300
	180	18.60	13.40	0.257	19.99	3.000	-3.070	0.261	-1.320
50	30	22.90	13.36	0.228					
	60	19.50	13.33	0.214	21.20	3.050	-2.180	0.221	-1.510
	90	16.60	13.31	0.206	18.05	2.900	-2.330	0.210	-1.560
	120	14.20	13.22	0.166	15.40	2.720	-2.530	0.186	-1.680
	180	10.50	13.13	0.134	12.35	2.510	-2.790	0.150	-1.900
70	10	20.89	13.05	0.111					
	20	18.62	13.02	0.105	19.76	2.980	-1.480	0.108	-2.230
	30	16.60	13.00	0.101	17.61	2.870	-1.600	0.103	-2.270
	60	11.76	12.98	0.099	14.18	2.650	-1.830	0.100	-2.300
	90	7.940	12.95	0.091	11.35	2.450	-2.060	0.095	-2.350
100	15	15.07	12.83	0.0668					
	30	10.47	12.81	0.0662	12.77	2.680	-1.180	0.0665	-2.710
	45	7.240	12.79	0.0642	8.860	2.210	-1.700	0.0652	-2.730
	60	5.770	12.67	0.0468	6.510	1.920	-2.080	0.0555	-2.890

Table 5 Order, rate constants, activation energy of delignification reaction of wheat straw

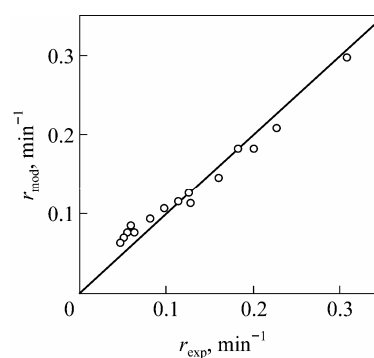
Temperature, °C	Order of reaction for lignin	Order of reaction for $[\text{OH}^-]$	Rate constants, $L^{0.34} \cdot \text{mol}^{-0.34} \cdot \text{min}^{-1}$	Correlation coefficient	Activation energy, $\text{kJ} \cdot \text{mol}^{-1}$	Frequent factor, $L^{0.34} \cdot \text{mol}^{-0.34} \cdot \text{min}^{-1}$
30	0.8477	0.2823	0.0053	0.9970	29.75	7.602×10^2
50	0.8889	0.3333	0.0124	0.9950		
70	1.018	0.3363	0.0233	0.9980		
100	1.089	0.4006	0.0491	0.9980		

kinetics model compared to experimental value with 9.47% of root-mean-square error are shown in Fig.3.

**Figure 2** Temperature dependence of rate constant

5 CONCLUSIONS

In this work, the pulping of wheat straw with NH_4OH - KOH aqueous solution was investigated. It was observed that instead of using the conventional alkaline pulping method, pulping of wheat straw with aqueous ammonia containing a small amount of KOH removed lignin effectively. The resulting black liquor

**Figure 3** Comparison r_{exp} with r_{mod}

contained nutrient elements such as nitrogen, potassium and ammoniacal lignin that can be used as fertilizer for agricultural production and this may alleviate the black liquor pollution issue.

It was determined the optimal pulping conditions for pulping with a degree of delignification of 85.12% and a pulp yield of 49.65% resulted. The delignification occurred in three phases: bulk delignification phase (from the beginning of cooking to 100°C), supplementary delignification phase (100°C to 155°C

and for 45min), and residual delignification phase (till the end of cooking).

The kinetics of delignification was evaluated and the delignification reaction is found to be first order with respect to residual lignin and 0.34 order with respect to $[\text{OH}^-]$. The activation energy is $29.75\text{kJ}\cdot\text{mol}^{-1}$

and the reaction rate equation is $-\frac{dL}{dt} = 7.602 \times 10^2$

$$\exp\left(-\frac{3577}{T}\right)L[\text{OH}^-]^{0.34}$$

NOMENCLATURE

C_1	mass of KOH per mass of oven-dry-wheat straw, $\text{g}\cdot\text{g}^{-1}$
C_2	mass of NH_3 per mass of oven-dry-wheat straw, $\text{g}\cdot\text{g}^{-1}$
E	activation energy, $\text{kJ}\cdot\text{mol}^{-1}$
K	reaction rate constant, $\text{L}^{0.34}\cdot\text{mol}^{-0.34}\cdot\text{min}^{-1}$
k_0	frequent factor, $\text{L}^{0.34}\cdot\text{mol}^{-0.34}\cdot\text{min}^{-1}$
L	average L_b , $\text{g}\cdot\text{g}^{-1}$
L_t	content of residual lignin at time t , $\text{g}\cdot\text{g}^{-1}$
M	order of $[\text{OH}^-]$
N	order of delignification
$[\text{OH}^-]$	average $[\text{OH}^-]_t$, $\text{mol}\cdot\text{L}^{-1}$
$[\text{OH}^-]_t$	concentration of OH^- at time t , $\text{mol}\cdot\text{L}^{-1}$
R	reaction rate, min^{-1}
R_{LS}	the volume of cooking liquid to the mass of oven-dry wheat straw, $\text{ml}\cdot\text{g}^{-1}$
r_{exp}	delignification rate obtained by experiment
r_{mod}	delignification rate obtained by kinetics model
T	cooking temperature, $^\circ\text{C}$
t	reaction time, min
t_1	time to reach maximum temperature, min
t_2	time at maximum temperature, min

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