Cleaner Production of Wheat Straw Pulp

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Abstract: A pulping method using NH_4OH with less amount of KOH as cooking liquor on wheat straw was developed. KOH could reduce consumption of NH_3 and cooking time for its strong alkalinity. The effects of various pulping conditions such as composition of cooking liquor, liquid-to-solid ratio, maximum temperature, cooking time to the maximum temperature and cooking time at the maximum temperature were studied. Experimental results indicated that the rate of delignification was 85.12% and the pulp yield was 49.65% under suitable pulping conditions. It looks promising to use black liquor containing nitrogen, phosphorus, potassium and organic substance as fertilizer resources for agricultural production. A new pattern of ecological cycling may be set up between paper industry and farming.

Key words: cleaner production; pulping with NH_4OH and KOH; wheat straw; delignification
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1 INTRODUCTION

China is one of the largest non-wood pulping countries because of the shortage of forest resources. Usually pulp mills are located in the countryside in China and caustic soda or lime is used as cooking reagent, which produces high pH wastewater with high content of organic pollutants. Black liquor from straw digestion contains high content of silicate and is highly viscous, so it is difficult to recover alkali from the black liquor. The investment of alkali recovery apparatus and operating costs are very high, which is part of the reason that the straw pulp wastewater has not been treated entirely, and the effluents of some paper mills ruin farmland and damage aquaculture[1, 2].

Instead of the conventional alkaline process, ammonia sulfite pulping has been applied in paper industry since 1968 due to its black liquor containing nutrition, which can be used as fertilizers to the rice field. However, this technology was not widely used because of long cooking time, difficulty for bleaching and corrosion of apparatus. The use of aqueous ammonia for pulping was mentioned[3−5] to control pollution by black liquor. In this method, black liquor also contains rich nutrition such as nitrogen, phosphorous and organic substances and is a potential fertilizer resource for agricultural production. To date no industrial application is reported probably because of the disproportionately high consumption of ammonia and excessive cooking time.

For further development of this process, Kenji et al.[6] reported cooking rice straw with NH_4OH/KOH, and Loffe[7] cooked birch wood by using NH_4OH/O_2. The details of these reports, however, were not available in open literature. In this paper, a pulping technology using NH_4OH and less amount of KOH as cooking liquor on wheat straw was studied.

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2 EXPERIMENTAL

2.1 Chemical Composition of Raw Material

Wheat straw harvested from the suburban Shanghai was used as raw material. Its chemical composition and the extractives from the straw by cold water (23±2)°C, hot water (95~100)°C, benzene-alcohol and 1% NaOH respectively are listed in Table 1.

Table 1 Chemical composition of the wheat straw used (%)

Moisture	SiO_2 1)	Lignin 1)	Pentosan 1)	Cellulose 1)	Extractive by			
					Cold water	Hot water	Benzene-alcohol	1% NaOH
9.08	4.59	26.43	22.50	42.33	8.00	19.78	2.74	37.69

Note: 1) On the dry basis.

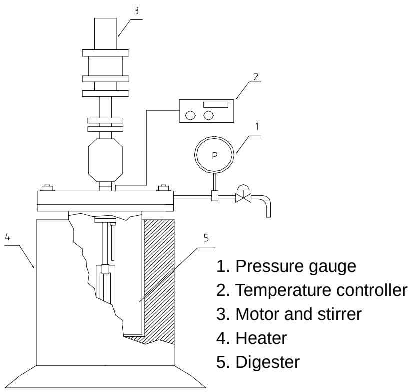


Fig.1 Sketch of the pressure digester

2.2 Pulping Procedure

The pulping was conducted in a 0.5 L stainless steel digester with an anchor stirrer (8 cm×3.5 cm) and a temperature controller. A sketch of the digester is shown in Fig.1. 25 g wheat straw cut to 2~3 cm long pieces was presoaked in the cooking liquor for 2 h, and then fed into the digester. The temperature was increased from room temperature to the preset maximum temperature and then kept constant for a given period of time. After cooking, the black liquor was separated from the pulp by filtration and the pulp was thoroughly washed with water. Then the pulp and black liquor were analyzed respectively. The lignin content in the raw material and pulp, weight of the raw material and pulp were determined according to the method in Reference [8]. Rate of delignification and pulp yield were calculated as follows:

$$\text{Rate of delignification} = \frac{\text{Lignin content in raw material} - \text{Lignin content in pulp}}{\text{Llignin content in raw material}} \times 100\%,$$

$$\text{Pulp yield} = \frac{\text{Weight of pulp}}{\text{Weight of raw material}} \times 100\%.$$

3 RESULTS AND DISCUSSION

3.1 Effect of the Composition of Potash Alkali

A pulping process that used aqueous ammonia with less amount of potash alkali as cooking liquor for rice straw was studied in our preliminary experiments. The potash alkali used was KOH and K_2CO_3. The positive effect of KOH was better than that of K_2CO_3[9]. Therefore, KOH was used in the following experiments.

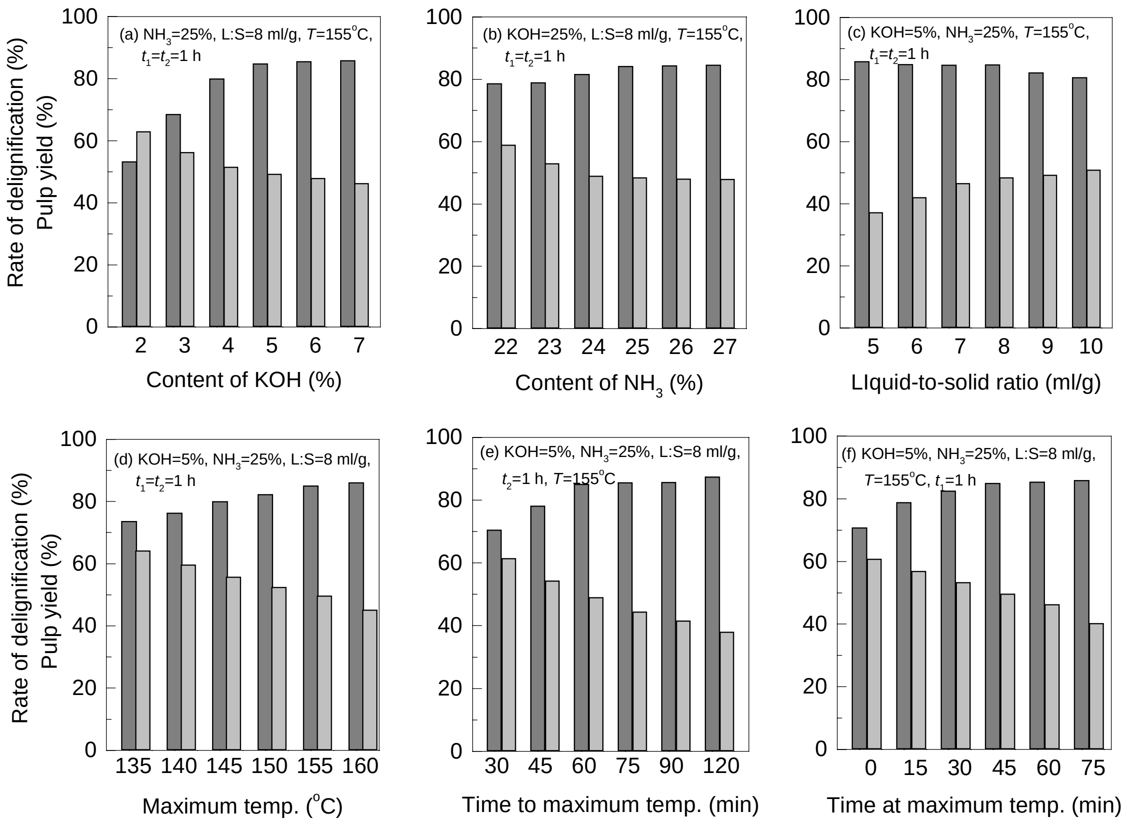
As KOH firstly reacted with lignin, the content of KOH had a remarkable influence on the delignification. As shown in Fig.2(a), the rate of delignification is 85.47% when the content of KOH reaches 5%, thereafter, the rate keeps constant. Pulp yield decreases continuously with increasing content of KOH because of cellulose and hemicellulose degradation. Therefore, the content of KOH was determined to be 5%.

3.2 Effect of the Content of NH_3

Although NH_3 is a weak alkali, the content of NH_3 was high and it reacted continuously with lignin during the cooking process. From Fig.2(b), the rate of delignification and the pulp yield are 85.17% and 49.26% respectively when the composition of NH_3 is 25%, and the suitable content of NH_3 was determined at 25%. The excessive NH_3 can be easily recovered in a recycle process.

3.3 Effect of Liquid-to-solid Ratio

Liquid-to-solid ratio influenced alkalinity of cooking liquid and homogeneous mixing of wheat straw. Figure 2(c) shows that the rate of delignification keeps constant when the ratio is less than 8, but it decreases gradually when the ratio is more than 8. When the ratio is less than 7, a small amount of raw material could not be changed into pulp because of not being soaked thoroughly, which resulted in a decrease of pulp yield. The liquid-to-solid ratio was set at 8.



Rate of delignification, Pulp yield, t_1: cooking time to the maximum temperature, t_2: cooking time at the maximum temperature

Fig.2 Effects of cooking parameters on rate of delignification and pulp yield

3.4 Effect of Maximum Temperature

The determination of the maximum cooking temperature should be considered comprehensively.

According to Fig.2(d), increasing the maximum temperature favours the delignification when the temperature reaches 155°C, and the rate is 85.16%, then it keeps constant despite of temperature increasing. On the otherhand, cellulose and hemicellulose are degraded rapidly over 155°C. Therefore, the maximum temperature was determined to be 155°C.

3.5 Effect of Cooking Time to Maximum Temperature

The bulk of lignin was dissolved into the black liquor during the cooking time to the maximum temperature. In Fig.2(e), the rate of deliginification increases with longer cooking time to the maximum temperature. On the other hand, when the cooking time to the maximum temperature is too long, the pulp yield would decrease because of cellulose and hemicellulose degradation. Therefore, the cooking time to the maximum temperature was determined to be 60 min.

3.6 Effect of Cooking Time at Maximum Temperature

An objective of cooking at the maximum temperature was to achieve a high rate of delignification. Most of lignin (79%) was removed during the cooking time to the maximum temperature. Only a fraction of residual lignin (5.7%) was removed during the cooking time at the maximum temperature. The increase of cooking time at the maximum temperature would increase slightly the rate of delignification. On the contrary, it would decrease pulp yield if the cooking time at the maximum temperature were kept too long. According to Fig.2(f), the pulp yield decreased clearly from 49.65% to 40.32% when the cooking time at the maximum temperature was increased from 45 min to 75 min. So the cooking time at the maximum temperature was determined to be 45 min.

3.7 Comparison Among NH_4OH–KOH, Soda–AQ and Ammonia Sulfite Pulping

The comparison among Soda–AQ, NH_4OH–KOH and ammonia sulfite pulping of wheat straw is listed in Table 2. As seen from Table 2, the results of NH_4OH–KOH and ammonia sulfite pulping of wheat straw are similar to those of the conventional Soda–AQ pulping process, the difference of delignification is small, but the pulp yield is higher than that of the conventional process. The black liquor from NH_4OH–KOH pulping consists of nitrogen, phosphorus, potassium and organic substance, and it can be used as fertilizer resources for agricultural production.

Table 2 Comparison among NH_4OH–KOH, Soda–AQ and ammonia sulfite pulping of wheat straw

	NaOH–AQ[10]	NH_4OH–KOH	$(NH_4)_2SO_3$–NH_4OH[10]
NH_3 (%)		25	
KOH (%)		5	
NaOH (%)	12		
AQ (%)	0.04		
$(NH_4)_2SO_3$ (%)			15
NH_4OH (%)			2.60
Ratio of liquid to solid (ml/g)	8	8	8
Maximum temperature (°C)	155	155	165
Cooking time to the maximum temperature (min)	60	60	180
Cooking time at the maximum temperature (min)	45	45	60
Pulp yield (%)	40.87	49.65	52.42
Rate of delignification (%)	86.45	85.12	84.97

Lignin molecule of wheat straw contains phenolhydoxyl, carbonyl and methoxyl[10]. During the pulping process, all these functional groups could react with alkali to produce dissolvable salts, which renders lignin to dissolve from fiber materials. Aqueous ammonia is a weak alkali, and when aqueous ammonia was used as cooking agent alone, the pulping process was uneconomic and impractical because of the large quantity of ammonia (35%) used and excessive cooking time (6 h)[3]. It was discovered in our experiment that with adding KOH, not only could the quantity of NH_3 be reduced to 25% and the cooking time be dramatically reduced to less than 2 h, but also potassium was provided for ammoniacal lignin. It showed that KOH could accelerate the delignification process. During pulping, hydroxyl of lignin reacted with KOH and NH_4OH one after another, which made large molecule of lignin degraded into small molecules and dissolved in alkali solution to form ammoniacal black liquor.

3.8 Utilization of Ammoniacal Black Liquor for Agricultural Resources

Comparative data on physical and chemical indexes of black liquor between NH_4OH–KOH and ammonia sulfite pulping are listed in Table 3. For both of pulping, many organic compounds of wheat straw were dissolved into the cooking liquor to form an ammoniacal black liquor after cooking, the discharge of the ammoniacal black liquor of NH_4OH–KOH pulping was approximate 10.9 m^3/t pulp. From Table 3, the pollutant load such as COD_{cr} and BOD_5 of black liquor of NH_4OH–KOH and ammonia sulfite pulping was lower than those of the conventional alkaline process.

Table 3 Comparison of black liquor between NH_4OH–KOH and ammonia sulfite pulping

Indexes	NH_4OH–KOH	Ammonia sulfite[13]
pH	8.45	6.8~8.2
Solid matters (g/L)	52.3	130~154.2
SiO_2 (g/L)	1.57	
Lignin (g/L)	27.3	
SS (mg/L)	798	
COD_{cr} (mg/L)	58414	130000~145000
BOD_5 (mg/L)	7460	16603~18519
Total nitrogen (g/L)	13.0	11.3~11.6
Total phosphorus (mg/L)	1.13	4.35~5.23
Total potassium (g/L)	6.65	1.1~2.1

Note: Testing methods of other indexes are showed in References [7,12].

The black liquor of ammonia sulfite pulping contained nitrogen, phosphorus, potassium, sulfur and organic matters that are potential fertilizer for agricultural production, but SO_4^{2-} in the black liquor is harmful to soil. Further, how to eliminate H_2S which is produced from black liquor in the process of storage and transport has not been solved thoroughly by now. But the black liquor of NH_4OH–KOH pulping containing elements and anions is beneficial to soil.

It is known that lignin is a kind of high polymer, and its tridimensional network structure results in its slow degradation. In our pulping process, this black liquor after recovery of excessive NH_3 contained a certain amount of nitrogen and potassium linked with benzene rings of lignin, which could be applied as slow-released nitrogen and potassium fluid fertilizer to the fields directly. Another use of the black liquor is that ammoniacal lignin is precipitated by coagulation while nitrogen and potassium on ammoniacal lignin are not displaced, then the precipitation could be processed to organic solid fertilizer for agricultural production by chemical modification, and the wastewater after the precipitation can be utilized as reuse water. The environmental pollution of black liquor could be solved after serious further development work and a new ecological pathway might be set up between paper industry and farming.

4 CONCLUSIONS

(1) The pulping technology with NH_4OH–KOH could remove effectively the lignin of wheat straw. The optimum pulping conditions are as follows: contents of KOH and NH_3 5% and 25% respectively, ratio of solid-to-liquid 8, the maximum temperature 155^{o}C, cooking time to the maximum temperature 1 h and the cooking time at the maximum temperature 45 min.

(2) With adding KOH, not only could the quantity of NH_3 be reduced to 25% and cooking time be dramatically reduced to about 2 h, but also potassium is provided for ammoniacal lignin. So KOH can accelerate the delignification process, quite different from ammonia sulfite pulping.

(3) An important advantage of this pulping method is that the black liquor contains rich nutrition such as nitrogen, phosphorus, potassium and organic substance that could be used as fertilizer resources for agricultural production.

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