Cleaner Production of Wheat straw Pulp with Potash

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A pulping method using KOH-K_2SO_3-AQ system as cooking liquor on wheat straw was studied in this paper. Digestion quantities on pulp yield and hardness during cooking was discussed and determined. It looks promising to use effluents of cooking into fertilizer because it contains rich nutrition such as potassium and lignin. A new pattern of ecological cycling may be set up between paper industry and farming.

Key words:
KOH-K_2SO_3-AQ system; cooking; wheat straw; ecological cycling

Introduction

Crop straw is one of the most abundant renewable resources in the world, but paper made from crop straw contributes to less than 8 % of global paper production.[3] The main reason is that black liquor from straw digestion has a high content of silicate and high viscosity. This leads to low alkali recovery ratio and high costs to black liquor disposal. Effluents from paper industry have become the largest contaminants on environment in China. However, the pulp output is insufficient to meet the increasing demand for paper, particularly in the developing countries. This results in an increasing shortage of wood raw materials and gradual deforestation of some areas in China. Therefore non-wood materials such as wheat straw and various other agricultural residues are so abundant and especially attractive for pulp-making. Nowadays, paper made from crop straw still contribute 60 % to total output in Chinese paper industry despite the fact that the Chinese government had cracked down large number of paper mills due to pollution from black liquor. Pollution from black liquor has been the most serious factor which hinders development of pulp and paper industry in China.[10]

Potassium-base chemical pulp of agricultural residues offers a novel approach to dispose of spent pulp liquor in a safe and economical way. Foelkel and Milanez[6] studied the use of chemicals where sodium was substituted by potassium in kraft and soda pulping of *Eucalyptus*. Their test result indicated that a satisfactory pulp could be obtained with K-based pulping chemicals. H'ng[4] reported that good pulp yield and low kappa number were achieved in potassium hydroxide-anthraquinone (KOH-AQ) pulping of oil palm fibers comparable to that of soda pulping. The pulp has a better beatability and brightness than the corresponding pulping from soda cooking. Recently, Nolan[2] reported that K-base has more efficient delignification ability than conventional Na-base pulping. Subsequently, Arbokem Inc[2] (Canada, 1991) proposed a pulping system using K_2SO_3, in which the spent liquor can be recovered into valuable K-fertilizer. In some developing countries such as China, straw-pulp still domainates the market of paper industry. K-base pulping could be a new approach to control pollution from black liquor.

A new pulping technique was studied in this article that using KOH-K_2SO_3-AQ system as cooking liquor to digest wheat straw. The purpose of this pulping system is to eliminate pollution by black liquor from straw-pulp without changing the main pulping technique during pulping production in China. The important advantage of this cooking system lies in its effective recovery system. Effluents of this cooking system could be transformed into inorganic or organic fertilizer by means of alkali recovery apparatus and cleaner production might be set up in the straw-pulp mills.

Material and methods

2.1 Wheat straw was obtained from the suburb of Beijing. Its composition was determined according to reference 5 and is listed below: ash content 7.69 %, nitric acid/ethanol cellulose 41.25 %, klason lignin 16.38 %, acid-soluble lignin 2.29 %, total lignin 18.67 %, cold water-solubles 11.82 %, hot water-solubles 17.63 %, 1 % NaOH-solubles 42.53 %, ethanol/benzene extractable 2.74 %, and poly-pentose 22.94 %.

2.2 Pulping experiments were carried out in 15 L stainless steel autoclave rotated digester which

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contains four 1 L reactors. Wheat straw was cut to 2–3 cm long pieces and was presoaked in the cooking liquor for 2 h, and then fed into the reactors. 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 (100 mesh) and the pulp was thoroughly washed with water. Then the pulp and black liquor were analyzed respectively. Kappa number, pulp yield, burst index, and tear index were determined according to the methods in reference 5.

Results and discussions

Effect of total alkali charge and alkali mass fraction on pulp yield and hardness

Total alkali charge is the total amount of KOH and K_2SO_3 (expressed as Na_2O to 100 g oven-dry wheat straw). Alkali mass fraction is KOH ratio, namely, $\frac{m_{KOH(Na_2O)}}{m_{KOH(Na_2O)} + m_{K_2SO_3(Na_2O)}}$.

This cooking system is mainly alkaline pulping cooperated with sulfite pulping. The dosage of KOH is the key factor in the course of delignification. From Fig. 1, kappa number and pulp yield falls sharply with the increase total alkali charge. This indicates that high alkali charge can effectively accelerate delignification and cellulose depolymerization, which results in the decrease of pulp hardness and yield. A satisfactory pulp was obtained when total alkali charge was 11 % and alkali mass fraction was 0.6, whose pulp yield is 58.8 % and kappa number is 18.8. It can be determined 11 % (Na_2O) of alkali charge and 0.6 of alkali mass fraction was the better dosage in this experiment.

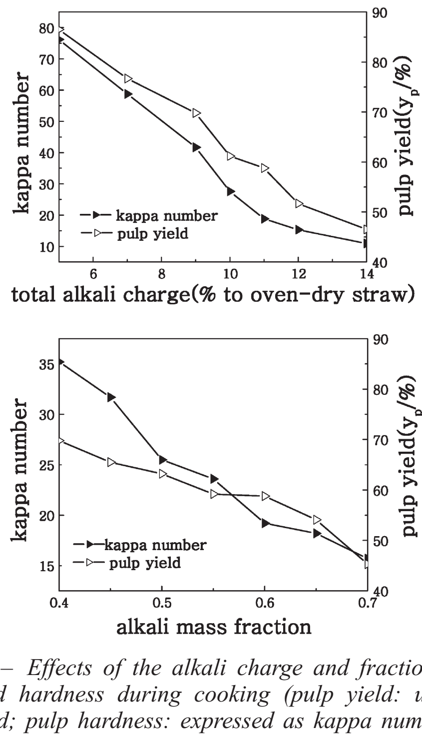


Fig. 1 – *Effects of the alkali charge and fraction on pulp yield and hardness during cooking (pulp yield: unscreened pulp yield; pulp hardness: expressed as kappa number)*

Effect of digestion temperature and digestion time on pulp yield and hardness

The determination of the maximum cooking temperature (T_{MAX}) and the cooking time at maximum temperature (T_C) should be considered comprehensively. In this experiment, we adopted 60min[7] the time to maximum temperature to determine T_{MAX} and T_C. It was observed from Fig. 2 that T_{MAX} and T_C had significant effect on pulp yield and hardness. Carbohydrate degradation which occurred at highest T_{MAX} and longest T_C greatly dropped pulp yield whereas variations of kappa number was not notable. According to Fig. 2 can be seen, in order to obtain satisfactory pulp yield, 160 °C (pulp yield 58.8 %) should be optimal maximum temperature and 100 min (pulp yield 58.8 %) should be the best time at maximum temperature from analyzing Fig. 2 under the condition of 11 % of total alkali charge(Na_2O) and 0.6 of alkali mass fraction.

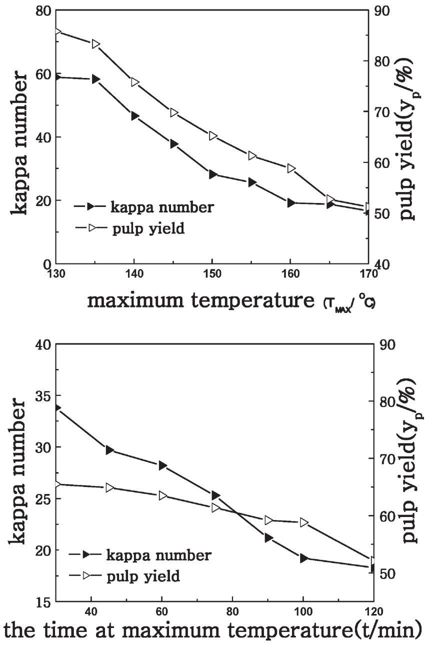
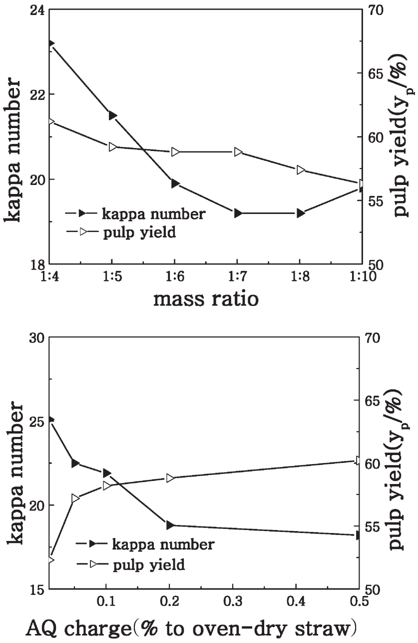


Fig. 2 – *Effects of the digestion temperature and time on pulp yield and hardness during cooking (pulp yield: unscreened pulp yield; pulp hardness: expressed as kappa number)*

Effect of AQ and solid-to-liquid ratio on pulp yield and hardness

Mass ratio (solid-to-liquid ratio) influences alkalinity of cooking liquid and homogeneous mixing of wheat straw. From Fig. 3, pulp yield and hard-



F i g . 3 – *Effects of AQ and mass ratio on pulp yield and hardness during cooking (pulp yield: unscreened pulp yield; pulp hardness: expressed as kappa number)*

ness decrease with the increase of mass ratio. 1:10 mass ratio increases pulp hardness a little because of decreasing alkalinity of cooking liquor. 1:7 should be the best mass ratio. Additional reagent AQ at low fraction (0.05 %) can effectively decrease pulp hardness and increase pulp yield (Fig. 3). But with increasing concentration of AQ, the increase of pulp yield and decrease kappa bumber wasn't notable. In the experiment, 0.2 % of AQ charge is optimal dosage.

Optimal techniques of cooking

The optimal technical condition in this cooking system is listed below: 11 % total alkali charge (Na_2O), 0.6 alkali mass fraction, 160 °C maximum temperature, 100 min the time at maximum temperature, AQ charge 0.2 % and 1:7 mass ratio. The result of cooking was achieved that pulp yield is 58.8 % and kappa number of pulp is 18.8. Variations of pulp yield and hardness depend mainly on the total alkali charge and alkali mass fraction. T_{MAX} and T_C had a secondary effect on pulping process. AQ charge and mass ratio had only minor effect on the degree of delignification. Among these factors, KOH charge is the most important factor which can reduce maximum temperature and time at maximum temperature with increasing content of KOH.

Comparison among Soda-AQ KOH-AQ and KOH-K_2SO_3-AQ pulping of wheat straw

From table 1 we can see, with the equal mole ratio, pulp yield and hardness from KOH-AQ is

T a b l e 1 – *Comparison between soda-AQ KOH-AQ and KOH-K_2SO_3-AQ pulping of wheat straw*

	Soda-AQ	KOH-AQ	KOH-K_2SO_3-AQ
NaOH (w/%)	13	–	–
KOH (w/%)	–	18	13
K_2SO_3 (w/%)	–	–	10
AQ (w_{AQ}/%)	0.2	0.2	0.2
Maximum temperature (T_{MAX}/°C)	155	155	160
The time to maximum temperature (t/min)	60	60	60
The time at maximum temperature (t/min)	60	60	100
Mass ratio	7	7	7
Unscreened pulp yield (y_u/%)	51.5	54.5	58.8
Screened pulp yield (y_s/%)	39.2	42.7	45.5
Kappa number	18.7	16.2	18.8
Whiteness of raw pulp (w/%)	51.7	54.5	47.8
Pulp viscosity (mPa·s)	72.3	89.6	82.5
Burst index (kPa·m^2/g)	2.32	2.78	3.01
Tear index (mN·m^2/g)	5.05	5.25	5.33

better than that of soda-AQ. This shows that efficiency of delignification of K-base pulping is higher than that of Na-base. Cooking system of KOH-K_2SO_3-AQ can obtain satisfactory kappa number and higher pulp yield. Burst index and tear index in K-base pulping is better than that of Na-base except higher pulp viscosity in K-base pulp. As a whole, properties of K-base pulp excelled or resembled to conventional Na-base pulp.

Advantages of KOH-K_2SO_3-AQ system and utilization of K-rich black liquor in agriculture:

AS-AQ (Alkaline sulfite-AQ) pulping has been applied widely in recent years and trends to substitute conventional Kraft pulping in straw-pulp industry. Under comparable pulp intensity, higher pulp yield and lower kappa number are obtained. Pulp washing and bleashing is easier to in the AS-AQ pulping process than that of Kraft pulping. This is because the aldyde group of end of cellulose or hemicellulose is oxidated by sulfite which prevents peeling reactions during cooking and increases pulp yield.[7]

Effluents of K-base cooking system are rich in potassium and lignin which can be used organic and inorganic K-fertilizer. Conventional Kraft pulping is little difference of solubility between Na_2SO_4 and Na_2CO_3(all about 45 g/100 g water at 100 °C) in green liquor. However, the solubility of K_2CO_3 and K_2SO_4 differs significantly (154 g/100 g water for K_2CO_3 and 20 g/100 g water for K_2SO_4 at 100 °C respectively). It is easy to separate K_2SO_4 from K_2CO_3 in green liquor according to difference of solubility. Not only can it form K-fertilizer (K_2SO_4), but also K_2CO_3 can be converted into K_2SO_3 by reacting with SO_2 or KOH with the process of causticization, which can avoid secondary pollution of white mud from sulfate.

Lignin is the second natural reuseable organic compounds, just behind cellulose. It is hard to be decomposed by microorganism owing to its complex tredimension network structure and its high C/N ratio(C/N250).[8] Lignin is also excellent meliorating reagent of soil due to its in the formation humic substances in soils.[8] So lignin can act as inert carrier for slow-released fertilizer because it can be degraded by microorganism slowly to release nutrients. Lignin is the main component in black liquor through delignification from wheat straw. At present how to convert black liquor into organic fertilizer has been becoming studying hotspot.

In the course of study of converting black liquor into organic slow-release fertilizer, $(NH_4)_2SO_3$ and NH_3 pulping were applied.[9] But these methods has vital defect that cooking pulp was hard to be washed and bleached. Properties of K-base pulp are excelled or similar to traditional Na-base pulp. Study on K-base has risen up in recent years due to its preponderant recovery system than Na-base pulping system.[1~4] From Table 2 we can see there were rich potassium and lignin in K-base black liquor, gentle pH in effluents of KOH-K_2SO_3-AQ pulping system can use it irrigate directly. Effluents from K-base cooking also can be evaporated and concentrated to 40 % solid content by multi-effect evaporator. After ammoxidation and granulation, it can form high-value organic compound fertilizer which contain 20 % of potassium(K_2O), 25 % of organic nitrogen and 45 % of organic matters. This kind of fertilizer can be senior commodity due to its virtue of slow-release effect. Those K-fertilizer (organic fertilizer and K_2SO_4) can preferentially be applied to Cl-fear crop such as tobacco and fruit. It can eliminate pollution from black liquor, at the same time K-fertilizer can relieve high-cost from expensive K-base cooking reagent. The environmental pollution from black liquor could be eliminated after serious further development work. This pulping system just is suitable to small-and medium-size paper mills which vastly dispersed in Chinese country. An ecological cycling will be formed among crop, crop straw and paper mills.

Table 2 – *Comparison of black liquor between KOH-AQ and KOH-K_2SO_3-AQ pulping of wheat straw*

	KOH-AQ	KOH-K_2SO_3-AQ
pH	11.2	9.5
Solid matters (γ/g l^{-1})	60.12	58.35
Baume degree	6.1	5.3
COD_{cr} (γ/mg l^{-1})	62741	55019
BOD_5 (γ/mg l^{-1})	9113	7640
Solid suspend (γ/mg l^{-1})	824	798
Organic matters (γ/g l^{-1})	41.5	40.1
Effective alkali (γ/g l^{-1})	2.24	0.75
K_2SO_3 (γ/g l^{-1})	–	1.54
Lignin (γ/g l^{-1})	29.5	27.3
Total potassium (K_2O (γ/g l^{-1}))	16.16	16.88

Conclusion

(1) The optimal pulping conditions are as follows: total alkali charge 11 % (Na_2O), alkali ratio 0.6, the maximum temperature 160 °C, cooking time at the maximum time 100 min (mass ratio 1 : 7) and AQ charge 0.2 %. Pulp yield of this pulping system is 58.8 %; kappa number is 18.8.

(2) An important advantage of this pulping system is that the black liquor contains rich nutrition such as potassium and lignin that could be used as fertilizer resources for agricultural production.

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