Environmentally friendly pulping of rice straw to eliminate black liquor discharge

GUOLIN HUANG, XIZHEN LIANG, ZHONGSHENG CHEN, AND CUIZHEN LI

ABSTRACT: Rice straw pulping trials were carried out with aqueous ammonia mixed with caustic potash to eliminate problems associated with black liquor in nonwood pulping. This process likely can use the black liquor, which contains nitrogen, potassium, and ammoniacal lignin, as a fertilizer for agricultural production. Excess ammonia in the black liquor was recovered by batch distillation. The black liquor was further treated for reuse by coagulation under alkaline conditions. We studied the effects of flocculating conditions, such as dosage of 10% aluminum polychloride, dosage of 0.1% polyacrylamide, reaction temperature, and pH of black liquor to obtain suitable technological conditions. Analyses confirmed that major quantities of lignin and 23.7% nitrogen (dried basis), 6.2% potassium (dried basis) existed in the flocculating residues, so this is potentially a good solid fertilizer. The amount of delignification and the pulp screen yield for the process remained steady at 83%-85% and 38%-40%, respectively, when reusing the supernatant four times.

Application: The black liquor problem associated with nonwood pulping can potentially be turned into a benefit through this environmentally friendly rice straw pulping process.

Nonwood raw materials such as rice straw, wheat straw, bagasse, and bamboo have attracted more interest as partial pulp replacements for traditional wood raw materials. At present, China accounts for more than two-thirds of the nonwood pulp produced worldwide [1]. Rice straw, an agricultural residue, appears to be an effective alternative to wood raw materials. It constitutes the main source of paper raw materials in China, and significant research on rice straw pulping has been conducted internationally [2-4]. The absence of an adequate and economical treatment technique for the black liquor from rice straw pulping is a major problem restricting the increased use of rice straw as a raw material in the papermaking industry.

Wood and nonwood pulping processes generate large volumes of black liquor as by-products and wastes. The overall annual world production of black liquor is approximately 500 million metric tons [5]. Black liquor wastewater is a mixture of organic and inorganic materials, with very high amounts of total dissolved solids (TDS). TDS usually represent up to 15% of black liquor, and are composed of lignin derivatives, low molecular weight organics, and spent digesting chemicals. The chemical oxygen demand (COD) and biochemical oxygen demand (BOD) vary from 10 g/L to 120 g/L and from 6 g/L to 75 g/L [6], respectively. This makes black liquor one of the most difficult materials to handle in wastewater treatment processes.

Black liquor poses an economic and environmental hurdle for chemical recovery to the functioning of nonwood paper mills. Most of the nonwood paper mills in China are small scale and do not have enough capital to install recovery systems for black liquor. The high silica content in straw-type raw materials makes the black liquor difficult to process in the alkaline recovery process. The application of several other potential treatments, including membrane separation technology [5], electro-coagulation treatment [7], ultrafiltration/nanofiltration [8], and anaerobic treatment technology [9], on a large scale is debatable.

This study explored rice straw pulping without generating black liquor waste. The cooking liquor used is aqueous ammonia mixed with a small amount of caustic potash. The benefit of using such a cooking liquor mixture is that it reduces the cooking liquor cost and minimizes the need for the post-reaction treatment of black liquor. The pulping conditions were optimized based on a previous study [10]. The black liquor was then further processed for cooking reuse by coagulation under alkaline conditions, and optimal flocculating conditions have been developed.

METHODS

Test of chemical composition of rice straw

The rice straw used in this study came from Zhuhan, a suburban area in Shanghai, China. The rice straw fibers had an average length of 1.13 mm and a width of 12.5 mm. Typical chemical compositions of the rice straw were analyzed according to China National Standards (GB), with the following results:

- moisture = 8.90% (GB/T 2677.2 – 1993)
- silica = 11.23% (GB/T 2677.3 – 1981)
- lignin = 24.02% (GB/T 2677.8 – 1993)
- cellulose = 35.39% (GB/T 5515 – 1985)

Pulping process and typical pulping conditions

The pulping process was carried out in an electrically controlled heating and cooking digester. We cut 100 g of rice straw to 20-30 mm lengths, presoaked the samples with cooking liquor for 2 h, and then fed them into the digester. The cooking temperature was increased from room temperature to one of several preset temperatures over 1 h and was then kept constant for 0 to 100 min. Following this cooking process, the cooked pulp was filtered and thoroughly washed with water. The pulp was analyzed to determine delignification amount, pulp screen yield, and pulp tensile, tear, and burst indexes. The black liquor was analyzed for pH, COD, lignin content, and ammonia.

Typical pulping conditions used in this study were as follows: 100 g of rice straw (dry basis) was mixed with 5 g potassium hydroxide (KOH) and 25 g aqueous ammonia, and diluted to 600 mL with deionized water. The ratio of cooking liquor to rice straw (dried basis) was 6:1, with a maximum pulping temperature of 155°C for 60 min of heating, followed by a 45 min holding time at that temperature.

Experiments with the recovery of excess ammonia

A batch distillation system was set up for free ammonium recovery. The experiment was carried out under atmospheric pressure. The temperature at the lower portion of the distillation column was 104°C to 105°C. We used a constant reflux ratio and processed 1000 mL of black liquor. Different cuts were collected from the top of distillation column during the period of distillation based on the boiling points.

Coagulation of pulping black liquor

After recovering the free ammonia, the black liquor was treated by coagulation to minimize waste generation. A known dosage (4-14 mL/L black liquor) of aluminum polychloride (PAC; 10% solution used) and a known dosage (6-16 mL/L black liquor) of polyacrylamide (PAM) with molecular weight of 3 million (0.1 % solution used) were added to the black liquor by rapid mixing (150 rpm) with an electric stirrer for 2 min, followed by slow stirring (50 rpm) for 8 min. After the flocculating process, the supernatant and residues were separated by filtration and were analyzed separately.

Supernatant reuse after coagulation

The supernatant from the coagulation process was reused for pulping after the addition of extra ammonium hydroxide (NH_4OH)/KOH. We reused the solution three times to assess the reusability of the black liquor supernatant. The rice straw fiber quality from pulping and the residual amounts in the supernatants from cycle to cycle was monitored to assess the effects of the repeated reuse of black liquor.

Determination of the coagulation residues

Infrared spectra of the coagulation residues were recorded on a spectrophotometer by using pressed potassium bromide (KBr) pellets. Aluminum, nitrogen, and potassium contents in the residues were analyzed with a spectrometer and elemental analyzer.

RESULTS AND DISCUSSION

Pulp evaluation

Pulping with pure ammonia is likely to be uneconomical and impractical because of the large quantity of ammonia needed and the excessive cooking time. However, for rice straw pulping, Huang [11] indicated that the addition of a small amount of KOH could significantly alter the process. Compared with normal alkaline pulping of wood at higher temperatures of 165°C to 175°C [12], rice straw could be pulped more easily at a temperature of 155°C because of its loose lignin structure and higher porosity. The lower pulping temperature also can help to prevent cellulose depolymerization, which in turn helps to decrease the amount of dissolved hemicelluloses in the liquor. Hence, this rice straw pulping process with NH_4OH/KOH achieved a satisfactory screened pulp yield, with good quality. Typical rice straw NH_4OH/KOH pulping results were as follows:

- delignification = 84.65%
- kappa number = 13.6 (GB/T 1546-1989)
- pulp screen yield = 38.12%
- pulp tensile index = 48.3 N.m^2/g (GB/T 12660-1990)
- pulp tear index = 5.11 mN.m^2/g (GB/T 3704-99)
- pulp burst index = 1.36 kPa.m^2/g (GB/T 3704-99)

The pulp strength properties of the pulping process for rice straw were similar to those from conventional pulping processes using soda-anthraquinone (AQ) [13], alkaline sulfite (AS)-AQ [13] and organosolv (diethanolamine) [14]. However, this aqueous ammonia pulping process yielded a higher tear index.

The composition and major characteristic properties of the black liquor generated from this pulping process were as follows:

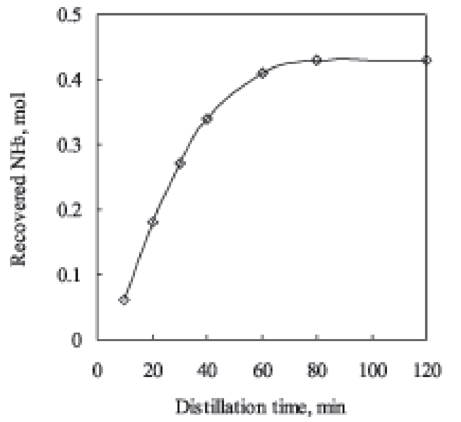
- pH = 11.5
- relative density = 1.042 (GB/T 4472-1984)
- silica content = 6.14 g/L (GB/T 18174-2000)
- lignin content = 17.6 g/L(GB/T 2677.8-1993)
- COD content = 57.9 g/L (GB/T14420-1993)
- ammonia nitrogen content = 16.1 g/L (GB/T 12763.4-1991)
- residual alkali = 1.04 mol/L

Recovery of excess ammonia from pulping black liquid

Figure 1 shows the molar concentrations of the ammonia in the collected distillates. The amount of ammonia recovered from 1000 mL of black liquor (in mol) increased with distillation time (up to 60 min; 0.42 mol of ammonia was recovered) because ammonia has high relative volatility under such conditions. After 60 min, the total ammonia recovery did not increase. The amounts of ammonia nitrogen and residual alkali after the ammonia distillation recovery process were 7.58 g/L and 0.58 mol/L, respectively.

Coagulation of pulping black liquor

In the coagulation process, PAC acted as a coagulant,



1. Recovered ammonia in liquor as a function of distillation time.

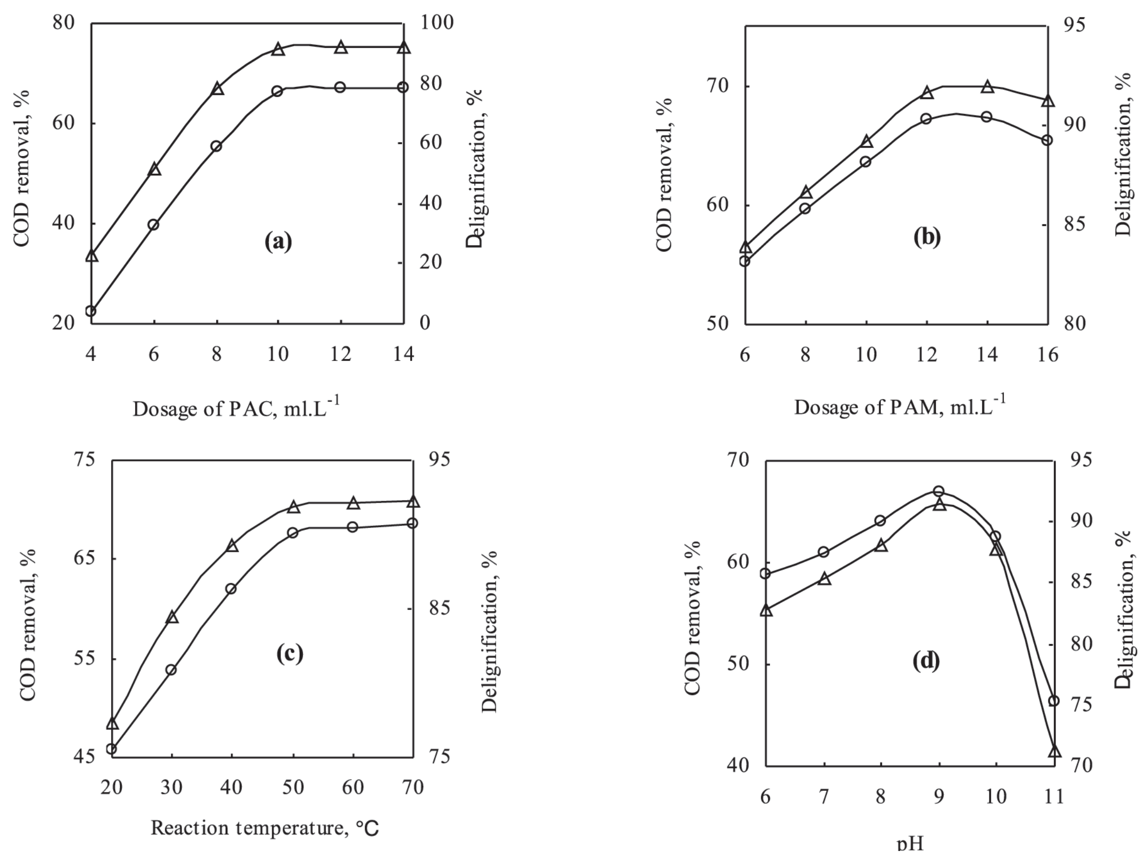
while PAM acted as an aid to flocculation. When PAC and PAM were used jointly, the synergistic effect helped the coagulation process for the black liquor. Each experimental condition was repeated three times to find the coefficient of variation of the experiment.

Effect of PAC dosage

To determine the effect of PAC dosage, we varied the dosage of 10% PAC from 4 mL/L to 14 mL/L black liquor. Other experimental conditions were as follows: 0.1% PAM of 14 mL/L black liquor, reaction temperature 50°C, and stirring time 10 min. **Figure 2a** shows the effect of the dosage of PAC on the flocculating process. The effect of coagulant dosage on destabilization depended on the operative destabilization mechanisms. When the amount of PAC increased from 4 mg/L to 10 mg/L, the amount of COD and lignin removal increased initially, and then remained constant above PAC amounts of 10 mg/L, which showed that a PAC dosage of 10 mg/L was enough for flocculation. Over-dosing aluminum sulfate causes settled colloids to be resuspended and restabilized in the system [15]. However, in this PAC/PAM black liquor coagulation process, particle resuspension and restabilization were not observed for PAC dosages over 10 mg/L. Hence, the optimal PAC dosage for black liquor coagulation was 10 mg/L.

Effect of PAM dosage

After choosing a constant 10% PAC dosage of 10 mg/L, the dosage of 0.1% PAM was varied from 6 mg/L to 16 mL/L black liquor. Other flocculating conditions were the same as those used in the investigation of PAC dosage. **Figure 2b** shows the effect of the PAM dosage on the flocculation process. Flocculation aids are normally added after destabilization by coagulants to speed up the aggregation rate. When the PAM concentration increased from 6 mg/L to 16 mg/L, the amount of COD and lignin removal increased slightly. Above a PAM



2. Effect of flocculating conditions on the treatment process.

concentration of 14 mg/L, the amount of removal dropped slightly. This peak value suggested that the optimal PAM dosage for black liquor coagulation was 14 mg/L.

Effect of reaction temperature

Using a 10% PAC dosage of 10 mg/L and a 0.1% PAM dosage of 14 mL/L, the reaction temperature was varied from 20°C to 70°C for the next experiment, and the stirring time was 10 min. **Figure 2c** shows the effect of reaction temperature on the flocculation process. The DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory can be applied to explain the effect of process temperature on coagulation [16]. Figure 2c also showed that the amount of COD and lignin removal increased at higher process temperatures, up to 50°C. For temperatures above 50°C, the amount of COD/lignin removal was virtually constant. The process of coagulation was very slow at low process temperatures. At higher process temperatures, the Brownian motion of the particles was enhanced, increasing the probability that the particles would collide and coagulate. On the other hand, higher process temperatures led to smaller precipitant sizes, and longer settling times. Thus, the optimal process temperature was 50°C.

Effect of pH

The next experiments were carried out at a 10% PAC dosage of 10 mg/L, a 0.1% PAM dosage of 14 mL/L, a reaction temperature of 50°C, and a stirring time of 10 min. The pH of the black liquor was adjusted from 6 to 11 with solutions of 1% sulfuric acid or 1% sodium hydroxide. **Figure 2d** shows the results. The COD and lignin removal increased at greater pH values from 6.0 to 9.0, after which COD/lignin removal began to decrease, and more significantly over a pH of 10.0. This suggested that the optimal pH of black liquor for coagulation was around 9.0.

Reusing black liquor after coagulation process

After the addition of extra NH4OH/KOH (to its initial concentration), the supernatant collected from treatment of rice straw pulping black liquor coagulation was reused for pulping. The reuse cycle was carried four times sequentially to assess the effect of reuse on the pulping yield. **Table I** summarizes the effects of black liquor reuse on the pulping process for rice straw. The amount of delignification and the pulp screen yield for the pulping of rice straw remained steady at 83%-85% and 38%-40%, respectively, when reusing the black liquor supernatant four times (with the addition of extra ammonia and KOH to give the proper ratio). Although the aluminum concentration in the supernatant increased gradually, the absolute amount was very small and had no detrimental effect on the cooking and the pulp quality.

Feasibility of using coagulation residues as an organic fertilizer

By substituting KOH/NH_4OH for sodium hydroxide as the cooking liquor, the resulting black liquor can be used as a fertilizer, offering an environmentally acceptable disposal alternative for this pulping residual. This solid material was analyzed for possible use as an organic fertilizer.

Lignin was generated in the pulping process, and the majority of lignin in the black liquor has been precipitated after the treatment process. Lignin itself also can be good for soil because it helps the soil to hold moisture, and it releases nutrients slowly as it decomposes. The spectra of the coagulation residue were recorded between 4000 and 400 cm^{-1} (**Fig. 3**). Peaks at 1600 cm^{-1}, 1510 cm^{-1}, and 1470 cm^{-1} appear on the residue, which are the typical absorption peaks of the aromatic organic matter.

Nitrogen and potassium are essential plant nutrients included in fertilizers [17,18]. The solid residual contained 23.73% nitrogen (dry basis) and 6.24% potassium (dry basis). According to Ma [19], this residue appeared to be a good organic solid fertilizer. The aluminum content was 0.24% (dry basis), which had no detrimental effect on the fertilizer. Most of the silica of rice straw was removed into black liquor. This could be explained as a dissolution process of silica in the alkaline solution with the formation of silicate.

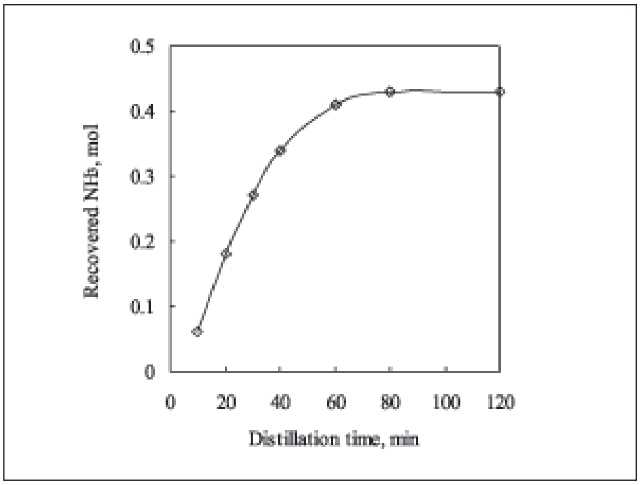
Rate of Delignification (%)		Pulp Screen Yield	Kappa Number	Composition of Black Liquor[1]			Composition of Supernatant[2]			
				Lignin (g•L-1)	COD_{cr} (mg•L-1)	pH	Lignin (g•L-1)	COD_{cr} (mg•L-1)	pH	Al (%)
I	85.63	38.64	13.87	33.2	70,459	9.28	2.96	19,333	9.15	0.058
II	85.47	38.89	15.66	33.8	70,867	9.41	3.11	19,847	9.21	0.063
III	84.76	39.47	17.59	34.4	71,004	9.50	3.19	20,368	9.26	0.079
IV	83.65	40.38	19.46	35.1	71,363	9.52	3.27	20,464	9.34	0.085

I = first recycling; II = second recycling; III = third recycling; IV = fourth recycling

1. Black liquid obtained after recycling; COD_{cr} determined by dichromate method

2. Supernatant; COD_{cr} determined by dichromate method

I. Effect of black liquor reuse on the pulping process.



3. The infrared spectrum of the sediment.

Further study is needed on the solid arising from coagulation using KOH/NH_4OH rice straw pulping as a fertilizer, to verify its potential as a fertilizer.

CONCLUSIONS

The pulping technique described in this report for reusing treated black liquor potentially could be used to eliminate problems with the discharge of black liquor. The black liquor from the pulping process contained rich nutrients of nitrogen, potassium, and significant amounts of lignin. After excess ammonia was recovered for reuse by batch distillation, the black liquor could be further treated by coagulation under alkaline conditions. The supernatant could be reused as part of cooking liquor and the coagulation residue from the process could be used as a fertilizer for agriculture production. It is an environmentally friendly rice straw pulping process. **TJ**

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Both wood and nonwood pulping processes generate large volumes of black liquor as by-products and wastes. Black liquor wastewater is a mixture of organic and inorganic materials, with very high amounts of total dissolved solids, chemical oxygen demand, and biochemical oxygen demand. This situation makes black liquor one of the most difficult materials to handle in wastewater treatment processes, so we chose to study this problem. This research also supports our previous research about NH_4OH/KOH pulping technology of rice straw. It is an environmentally friendly rice straw pulping process.

The most difficult aspect of this research was leakage of ammonia. Better sealing of the cooking equipment was needed to correct this problem.

There is a good prospect that this process can use the black liquor, which contains nitrogen, potassium, and ammoniacal lignin, as a fertilizer for agricultural production -- a most interesting finding. Mills might use the pulping technology to eliminate the black liquor problem.

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However, further study is needed on the solids arising from coagulation using KOH/NH_4OH rice straw pulping as a fertilizer, as a means to verify its potential as a fertilizer.

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