# Preparation of Fiber Raw Materials by Cooking Golden Bamboo Grass (*Arundo donax*) with Calcified Regenerated Alkali Solution

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The increasing consumption of paper products has led to a shortage of paper fiber raw materials. It is necessary to develop new plant materials to alleviate the shortage of fiber suitable for papermaking. In this study, the fast-growing plant golden bamboo grass (Arundo donax), which is cultivated and planted in Guangxi province of China, was used as a new material for pulping. The average pulp yield by cyclic-cooking method averaged 48.6%, being 4.1% greater than the pulp yield by the ordinary caustic soda method. Much of the increased yield was attributable to the reprecipitation of lignin onto the fibers. The paper properties of the pulp prepared by cycle-cooked method did not decrease significantly, compared with the pulp prepared by the usual single-cooked method. Therefore, the pulp met the requirements of national standards of many kinds of papers. However, the pulp was not suitable for bleaching, due to its high consumption of oxidizing agents to reach the required brightness. Therefore, this research demonstrates that the fast-growing plant, Arundo donax is a good raw material for pulp, and the innovative method of cyclecooking method can significantly improve the pulp yield.

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#### INTRODUCTION

With rapid economic development, China has now become the world's largest paper and cardboard producer (Dai *et al.* 2023). In 2022, China's paper and cardboard output was 124.32 million tons (FAO 2023). Nevertheless, the Chinese pulp and paper industry is facing the dilemma of fiber shortage (Kaur *et al.* 2017), mainly the shortage of forest resources (Li *et al.* 2017; Shang *et al.* 2020).

Therefore, it is necessary to study new pulping raw materials (Lexa *et al.* 2023). Ferdous *et al.* (2021b) used the soda-anthraquinone pulping method, when the alkali dosage was 20%, and the pulp yield of banana stem, leaf, and pedicel was 30.0%, 34.6%, and 39.1%, respectively. Bhardwaj *et al.* (2019) studied that bagasse contained 40.4% cellulose, 33.2% hemicellulose, 17.4% lignin, and 6.45% ash. The soda pulping method was used for cooking, and the pulp yield was 46% under the condition of alkali dosage of 14%. In addition, some scholars have studied the application of plant fiber materials such as corn stalks (Mishra *et al.* 2020), durian peels (Masrol *et al.* 2017), palm oil empty fruit

bunches (Sharma *et al.* 2015), tobacco stalks (Shakhes *et al.* 2011; Wu *et al.* 2019), whole kenaf stem (Habashi *et al.* 2014), bamboo (Shen *et al.* 2018; Chen *et al.* 2021), rice straws (Lai *et al.* 2022), and cotton stalks (Hu and Nie 2014) in pulping and papermaking. These raw materials generally have problems such as low pulp yield (Ferdous *et al.* 2020; Ferdous *et al.* 2021a), seasonal supply (Abd El-Sayed *et al.* 2020), and storage difficulties (Gominho *et al.* 2018; Abdelmageed *et al.* 2019).

Predecessors have also studied the application of the papermaking direction of *Arundo donax*. Coelho *et al.* (2007) studied the lipophilic characteristics of giant reed australis. Such work will help to predict pitch problems during pulp and papermaking of this fiber. Iglesias *et al.* (2023) analyzed the chemistry and mechanics of *Arundo donax* pulp and found that it is suitable for papermaking materials and has the potential for bleaching. As a new crop cultivated from the improved varieties of *A. donax*, golden bamboo grass (GBG) has the characteristics of strong vitality, perennial, and high fiber yield. The main components were 40.1% cellulose, 16.0% acid-insoluble lignin, 25.5% pentosan, and 6.34% ash, and the fiber aspect ratio was 90.2. Therefore, it can be used as a new pulping and papermaking raw material.

Based on previous research (Nong *et al.* 2019, 2020 Li *et al.* 2021; Huang *et al.* 2022), this article used GBG as raw material. GBG chemical pulp was prepared through recycling cooking with the pulping wastewater treated by lime. In this work, the wood cooking wastewater was treated with lime directly to recover the alkali of sodium hydrate. Therefore, the regenerated alkali liquid here contains a part of the organic matter, after its removal from the lignin-containing raw material. Lignin from the pulping liquor is allowed to precipitate back onto the fibers, thus increasing the pulping yield. The properties of the generated pulp were tested and compared with that of the pulp prepared by the traditional process. As this research obtained good results, it showed GBG to be a good raw material for pulp, and recycling cooking wood by pulping wastewater was found to be an effective method to increase pulp yield. Therefore, this method broadens the types of raw materials for pulp and paper and enriches the theoretical basis for the pulp and paper industry.

#### EXPERIMENTAL

#### Materials

The GBG raw material was provided by Guangxi Agricultural Science and Technology Co., Ltd. The plant height was about 2.8 m, with a stem diameter of about 1.5 to 2.0 cm, under a growth period of 3 months. It was cut into slices with an average length of 2.5 to 3.0 cm and a width of approximately 1.0 cm, and their wall thickness was about 0.3 cm. After outdoor air-drying treatment, the water content was about 7 to 9 %. Then, it was placed in a plastic sealed bag to balance moisture and used as a raw material for cooking experiments.

#### Methods

Recycled mixed alkali solution to prepare chemical pulp by cyclizing cooking GBG

Step I: The black liquor was treated with calcium oxide, and the additional amount was 50% of the solid content. After 3 h of reaction, the recovered mixed alkali liquor was obtained by filtration. The alkalinity (mass concentration of NaOH) values in the recovered mixed alkaline solution were detected, and the content of NaOH in the recovered alkaline solution was calculated (Nong *et al.* 2020).

Step II: Carrying out cyclic-cooking, the procedure is to put 50 g of absolutely dry GBG raw materials into the cooking pot, followed by the addition of recycled alkali (It accounts for about 25% of the total alkali content), fresh NaOH, and a certain volume of water required to achieve a solid-liquid ratio of 1:6. The heating curve was set as follows: The temperature was raised for 2 h under normal temperature conditions to reach 165 °C, then maintained at 165 °C for 2 h.

Step III: The black liquor obtained after cooking was returned to step I for cycle experiments, and a total of five cycles were performed. After cooking, the pulp was taken out and it was put into a pulp bag. It was fully washed in running water, and torn into small pieces after squeezing out the excess water in the pulp. The pulp was sealed in a plastic bag and balanced with water, preparing for the determination of pulp moisture content. Black liquor was recovered for later use. The cyclic-cooked process is shown in Fig. 1.

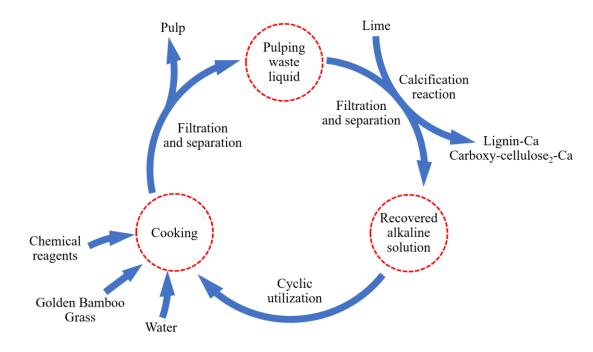


Fig. 1. Cyclic cooking process

Preparation of chemical pulp by single alkali cooking of GBG (As a comparison)

Step I: Add 50 g of absolutely dry GBG raw material to the cooking pot; the amount of alkali used is 20% of the absolutely dry raw material, that is 10 g of sodium hydroxide (NaOH); then add the required volume of water to the cooking pot to make the material-liquid ratio reach 1:6.

Step II: Set the heating curve: raise the temperature for 2 h under normal temperature conditions to reach 165 °C, then maintain the heating at 165 °C for 2 h.

Step III: After cooking, take out the pulp and put it into the pulp bag, fully wash it in the running water, tear it into small pieces after squeezing out the excess water in the pulp. The pulp was sealed in a plastic bag and balanced with water in preparation for the determination of pulp moisture content.

#### Bleaching methods of pulp

Ten g of absolutely dry GBG pulp was weighed. Sufficient deionized water was added to make the pulp concentration about 10%. Then, the 10% wet pulp was placed in a sealed bag for bleaching. After adding dilute sulfuric acid, the amount of chlorine dioxide was added in the amount of 6% of the absolute dry pulp for a 1.5 h reaction at 70 °C. In the bleaching process, the bags were taken out and kneaded gently every 15 min to allow the materials to react evenly (Ashori *et al.* 2006).

#### Calculation method of pulp yield

Three to four portions of wet pulp with a total mass of 0.5 to 0.7 g were taken out from the sealed bag after balancing the moisture content. The moisture rapid tester was used to determine the moisture content of the pulp. Each measured data was obtained as the average obtained from three measurements. The calculation method of pulp yield is as follows:

$$Pulp \ yield = \frac{Wet \ pulp \ weight \times (1-Moisture \ content \ of \ wet \ pulp)}{mass \ of \ material} \times 100\%$$
(1)

In Eq. 1, the pulp yield is the mass of the generated dry pulp divided by the mass of raw material multiplied by 100%. and the mass of the dry pulp is calculated by the mass of wet pulp multiplied by its solid content, which can be expressed as 1.0 minus the moisture content of the wet pulp.

#### Pulp performance testing methods

A HAAGE sheet former BB was used to make 80  $g/m^2$  paper and test the performance of the paper obtained by single-cooked method, cyclic-cooked method, and bleaching.

A series of tests was conducted on various properties of paper using a range of equipment, including the TMI 83-20 Tear Tester, L&W Tensile Tester, M.I.T Folding Endurance Tester, TMI EC3x Burst Tester, TMI Compression Tester, Technidyne ColorTouch PC, and Technidyne PROFILE/Plus Roughness & Porosity Tester. These tests were conducted in accordance with international standards such as ISO 1974 (2012), ISO 1924-2 (2008), ISO 5626 (1993), ISO 2758 (2014), ISO 12192 (2011), ISO 2470-2 (2008), and ISO 5636-3 (2013).

The tests focused on evaluating the paper's tearing strength, tensile strength, folding endurance, bursting resistance, pressure strength under environmental conditions, D65 brightness, and air permeability.

#### **RESULTS AND DISCUSSION**

#### Pulp Yield and Composition, Structure Analysis

Pulp yield of single-cooked and cyclic-cooked

To investigate the pulp yield generated by the cyclic cooking method, the mass of wet pulp and its moisture were tested. The calculated pulp yields are shown in Fig. 2. As shown, the pulp yield of single-cooked caustic soda pulping was 44.5%, and the average yield from cyclic-cooked caustic soda pulping was 48.6%, which was 4.1% higher than that of the former. It can be seen from the figure that the pulp yield increased from the initial 44.5% to 50.2% after the first three times of cooking (two cycles of cooking). The

yield of cooking pulp was stable at  $48.5 \pm 0.68\%$  after three cycles. These results indicated that chemical pulping can be used in GBG, and the cyclic cooking of calcified alkali recovery can improve the pulp yield of chemical pulping.

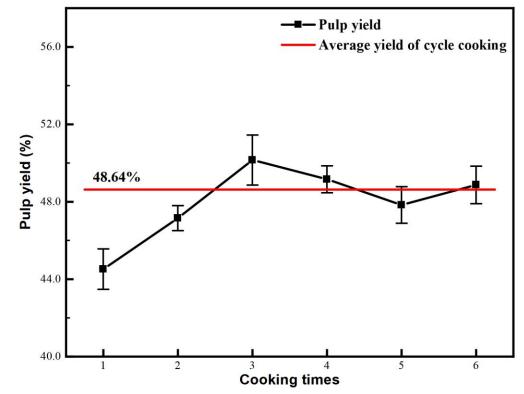


Fig. 2. The relationship between cooking times and pulp yield

#### Micro-morphology analysis of pulp

To understand the microstructure of the generated pulp, scanning electron microscopy (SEM) analysis of the pulp was performed, as shown in Fig. 3. Figure 3(a) shows the SEM images of the pulp samples obtained by single-cooked method, while Figs. 3(b, c) show images of the pulp obtained by cyclic-cooked method.

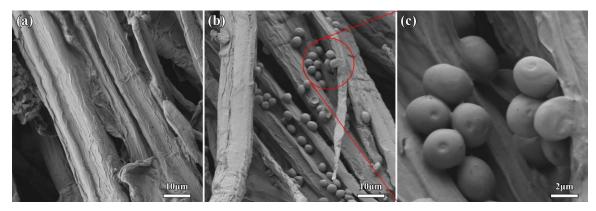


Fig. 3. SEM images of single-cooked (a) and cyclic-cooked (b, c) pulps

As shown in Fig. 3(a), there was almost no lignin and other small molecules attached to the cellulose surface on the tightly arranged surface of the cellulose. However, there was a great change apparent in Fig. 3(b), which shows some spherical particles

binding to the surface of the cellulose. The spherical small molecule structure is magnified as shown in Fig. 3(c). It is proposed that the spherical particles are mainly composed of lignin, which becomes attached to the cellulose surfaces. Precipitation of the lignin can account for the observed increase of pulp yield generated by the cyclic-cooked method.

#### X-ray photoelectron spectroscopy (XPS) analysis of pulp

To explore the elemental composition of the pulp, XPS analysis was performed. The XPS curves of the single-cooked(a) and cyclic-cooked(b) pulp samples are shown in Fig. 4. The XPS full spectrum of (a1) and (b1) was dominated by C1s and O1s peaks. The peak intensity of the two peaks of cyclic-cooked was significantly higher than that of single-cooked. The peak ratio of the carbon-oxygen peak of (a1) was 0.84, and the peak ratio of the carbon-oxygen peak of (b1) was 1.05. The carbon spectra of (a2) and (b2) mainly showed C1s, C-OR and COOH peaks. It can be seen from the peak intensity that the C1s peak of (b2) was significantly higher than that of (a2), and its C-OR and COOH peaks were not much different from those of single-cooked. This further shows that cyclic cooking can recycle the organic matter with high carbon-oxygen ratio in the circulating alkali liquor, thereby increasing the pulp yield. The contents of carbon, hydrogen, and oxygen in cellulose were 44.4%, 6.2%, and 49.4%, respectively (Wang et al. 2015; Fernandez et al. 2023). The ratio of carbon to oxygen content in lignin is about 3.00 (Chen et al. 2023). This XPS analysis demonstrated that some lignin had combined to the cellulose, which is consistent with the SEM analysis result. Therefore, it further demonstrates that some small molecular weight lignin combined with cellulose.

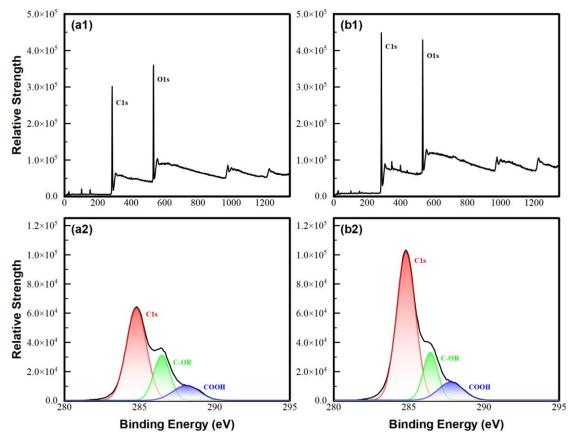


Fig. 4. XPS curves of single-cooked (a) and cyclic-cooked (b)

#### Infrared attenuated total reflection spectroscopic (ATR) analysis of pulp

To investigate the functional group content of the pulp, ATR analysis of the pulp was performed. The ATR curves of the single-cooked and cyclic-cooked pulp samples are shown in Fig. 5. The results showed absorbance peaks at 3645.7, 3525.8, 2883.9, 1747.0, 1689.4, 1638.0, 1574.4, 1538.3, 1424.9, 1160.4, 1100.6, 1029.6, and 671.3 cm<sup>-1</sup> in both single-cooked pulp and cyclic-cooked pulp.

The absorbance peaks at 3645.7 and 3525.8 cm<sup>-1</sup> are attributed to the stretching vibration of the OH group of the alcohol phenol; the absorbance peak at 2883.9 cm<sup>-1</sup> is attributed to the symmetric stretching vibration of the alkane CH group; the absorbance peaks at 1747.0 and 1689.4 cm<sup>-1</sup> are attributed to the stretching vibration of the aldehyde C=O group; the absorbance peaks at 1638.0, 1574.4, 1538.3, and 1424.9 cm<sup>-1</sup> are attributed to the stretching vibration of the benzene ring skeleton. The absorbance peak located at 1160.4 cm<sup>-1</sup> is attributed to the stretching vibration of the stretching vibration of the C-O group; the absorbance peak at 1100.6 cm<sup>-1</sup> is attributed to the stretching vibration of the C-O group of the aliphatic ether; the absorbance peak at 1029.6 cm<sup>-1</sup> is attributed to the stretching vibration of the C-O group of the saturated secondary alcohol; the absorbance peak at 671.3 cm<sup>-1</sup> is attributed to the out-of-plane bending vibration of the O-H group of alcohols (Strunk *et al.* 2011; Huntley *et al.* 2015).

After cyclic-cooked, the relative content of OH group, aldehyde C=O group, and benzene ring skeleton absorption peak of alcohol phenol were strengthened, which confirms that cyclic-cooked will increase the amounts of aromatic hydrocarbons and polysaccharides mixed into the pulp, thus increasing the yield of pulp. These ATR analysis results were consistent with the SEM analysis results. Therefore, it further demonstrates that some small molecular weight lignin was combined with cellulose by reprecipitation.

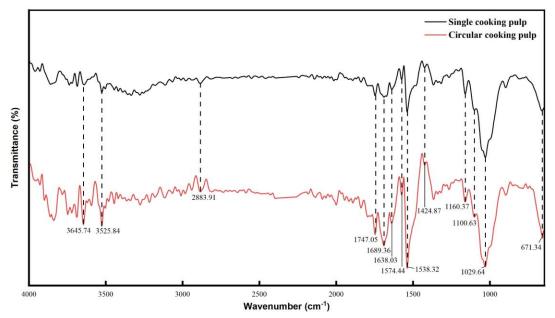


Fig. 5. ATR curves of single-cooked and circular-cooked pulps

#### Analysis of pulp cellulose, hemicellulose, and lignin content

To further analyze the reasons why cyclic cooking leads to the increase in the pulp yield, the NREL method was used to analyze the cellulose, hemicellulose, and lignin content of single-cooked and recycled pulps (Zheng *et al.* 2020). The analysis results are shown in Fig. 6.

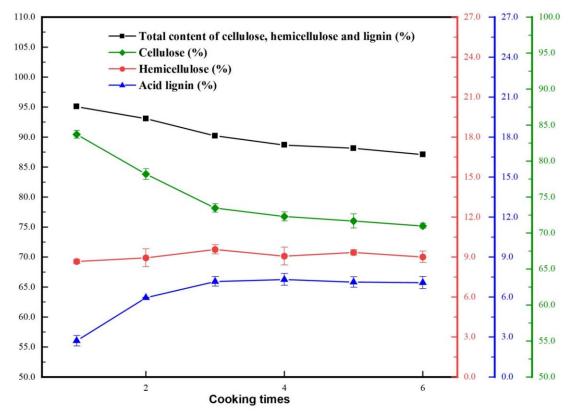


Fig. 6. Contents of cellulose, hemicellulose, and lignin in the pulp by single-cooking and cycle-cooking pulp

As shown in Fig. 6, the cellulose content dropped rapidly from 83.7% in first cooking to 73.5% in the third cooking, and then it slowly dropped to 71.0% after the sixth cooking. On other hand, the hemicellulose content rose from 8.7% in first cooking to 9.6% in the third cooking, and then stabilized between 9.0% and 9.3%. In addition, the acid lignin content increased rapidly from 2.7% in the first cooking to 7.2% in the third cooking, and then stabilized between 9.0% and 9.3%. In addition, the acid lignin content increased rapidly from 2.7% in the first cooking to 7.2% in the third cooking, and then stabilized between 7.0% and 7.4%. In summary, the total amount of cellulose, hemicellulose, and lignin decreased from 95.7% to 87.1% with the increase of cooking times. The reason may be that instead of cellulose, hemicellulose, and lignin, some other organic substances such as organic acids, resins, and alcohols, are precipitated and possibly polymerized with cellulose, leading to the decrease of the proportion of the three main components.

This analysis of the contents of lignin, cellulose, and hemicellulose indicates that some lignin has combined to the cellulose. This result is consistent with the SEM, XPS and ATR analysis results. Therefore, it further demonstrates that some small molecular weight lignin and other substances combined with cellulose by polymerization reactions, leading to the increase of the pulp yield.

#### Analysis of Pulp Bleaching Effect

To explore the bleaching effect of GBG pulp, the loss ratio and D65 brightness of the bleached pulp were analyzed. The results are shown in Fig. 7. Using the same dosage of chlorine dioxide for bleaching, the loss ratio was stable at around 6.2%. Due to the gradual superposition of the content of non-cellulose substances in the circulating cooking process, the bleaching effect gradually decreased. Its D65 brightness decreased from 66.5%

of the first cooking to 54.7% after cooking for the sixth time. The D65 brightness of the unbleached pulp gradually decreased from 26.0% to 21.7%. The results show that the single-cooked pulp was more suitable for bleaching (Ashori *et al.* 2006).

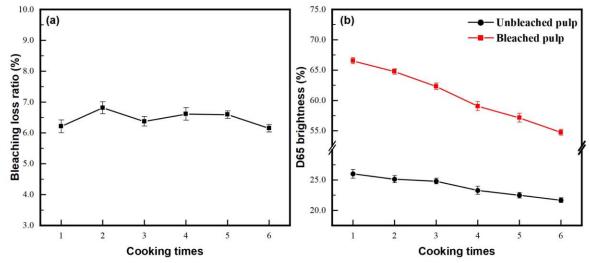


Fig. 7. Relationship between cooking times and bleaching loss ratio (a) and D65 brightness (b)

#### Analysis of Physical Properties of Paper

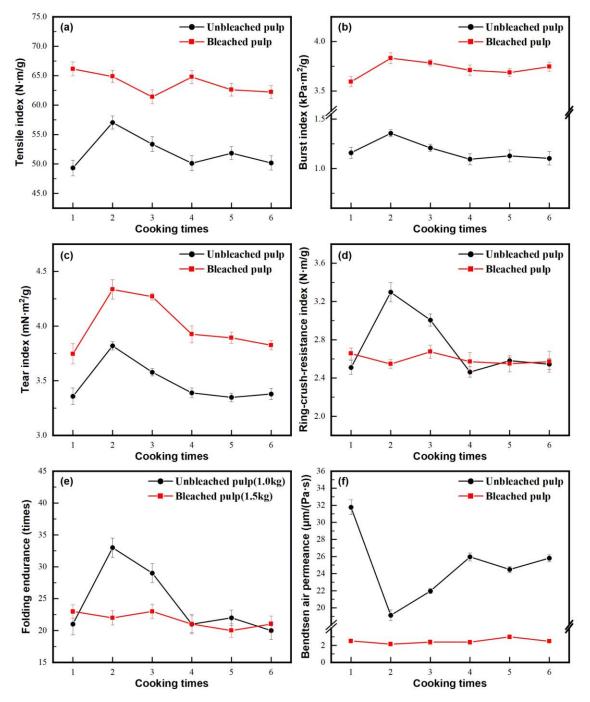
To understand whether the unbleached pulp and bleached pulp of single-cooked and cyclic-cooked requirements of papermaking, mechanical property tests of the pulp were conducted. The results are shown in Fig. 8.

From Fig. 8(a), the tensile index of the single-cooked unbleached pulp was 49.3  $N \cdot m/g$ ; the tensile index of unbleached pulp reached a max value of 57.0  $N \cdot m/g$  in the first cyclic-cooking, decreased to a certain extent in second and third cyclic-cooked batch, and finally stabilized at 50.2 to 51.8  $N \cdot m/g$ . The tensile index of each cooking bleached pulp was better than that of the unbleached pulp.

From Fig. 8(b), the burst index of single-cooked unbleached pulp was 1.16 kPa·m<sup>2</sup>/g; the burst index of unbleached pulp reached a max value of 1.36 kPa·m<sup>2</sup>/g in the first cyclic-cooked batch, decreased slightly in second and third cyclic-cooked batch, and finally stabilized between 1.09 to 1.13 kPa·m<sup>2</sup>/g. The burst index of each cooking bleached pulp was significantly higher than that of the unbleached pulp.

From Fig. 8(c), the tear index of single-cooked unbleached pulp was  $3.36 \text{ mN} \cdot \text{m}^2/\text{g}$ ; the tear index of unbleached pulp reached a max value of  $3.82 \text{ mN} \cdot \text{m}^2/\text{g}$  in the first cyclic-cooked batch, it decreased slightly in second and third cyclic-cooking, and finally stabilized at 3.35 to  $3.39 \text{ mN} \cdot \text{m}^2/\text{g}$ . The tear index of each cooking bleached pulp was higher than that of the unbleached pulp.

From Fig. 8(d), the ring-crush-resistance index of single-cooked unbleached pulp was 2.51 N·m/g; the ring-crush-resistance index of unbleached pulp reached a max value of 3.30 N·m/g in the first cyclic-cooked, decreased slightly in second and third cyclic-cooked, and finally stabilized between 2.46 and 2.58 N·m/g. The ring-crush-resistance index of each cooked bleached pulp was the same as that of the unbleached pulp.



**Fig. 8.** Relationship between cooking times and physical properties of unbleached pulp and bleached pulp paper sheets

From Fig. 8(e), the folding endurance of single-cooked unbleached pulp was 21 times (1.0 kg); the folding resistance of unbleached pulp reached a max value of 33 times (1.0kg) in the first cyclic-cooked, decreased to a certain extent in second and third cyclic-cooked, and finally stabilized between 20 and 22 times (1.0kg). The folding resistance of each cooked bleached pulp was significantly higher than that of the unbleached pulp.

From Fig. 8(f), it can be seen that Bendtsen air permeance of single-cooked unbleached pulp was  $31.8 \,\mu$ m/(Pa·s). Bendtsen air permeance of unbleached pulp reached

a minimum value of 19.13  $\mu$ m/(Pa·s) in first cyclic-cooked batch, increased to a certain extent in second and third cyclic-cooking, and finally stabilized at 24.5 to 26.0  $\mu$ m/(Pa·s). Bendtsen air permeance of each cooking bleached pulp was significantly lower than that of the corresponding unbleached pulp.

The physical properties of first and second cyclic-cooked paper were significantly better than that of single-cooked paper. After the performance of the cyclic-cooked paper was stable, there was no significant difference in the physical properties of single-cooked paper. This shows that cyclic-cooking procedure had little effect on the test performance. In addition to the ring crush index not increasing, the other physical properties measured by bleached pulp were significantly better than those of unbleached pulp, regardless of being single-cooked or cyclic-cooked.

Performance Index	Single-cooked		Circular-cooked		
	unbleached	bleached	unbleached	bleached	National Standards
macx	pulp	pulp	pulp	pulp	
					Premium product: ≥
Tensile					39.2ª, ≥15.0 <sup>b</sup> , ≥33.0 <sup>c</sup> , ≥
index	49.34	66.15	50.71	63.18	32.00 <sup>g</sup> , ≥35.00 <sup>h</sup> ; AAA: ≥
(N∙m/g)					49.0 <sup>d</sup> ; Qualified product: ≥50.0 <sup>f, i</sup>
Burst index (kPa⋅m²/g)	1.16	3.59	1.11	3.75	Premium product: $\geq$ 1.06 <sup>b</sup> , $\geq$ 3.50 <sup>e</sup> , $\geq$ 2.50 <sup>i</sup>
tear index (mN·m²/g)	3.36	4.34	3.37	3.88	Qualified product: $\geq 3.00^{a}$ , °, $\geq 2.80^{f}$
Ring-crush- resistance index (N·m/g)	2.51	2.66	2.53	2.58	Qualified product: $\geq$ 3.00 <sup>d</sup> , $\geq$ 5.00 <sup>e</sup>
Folding resistance (times)	21(1.0kg)	23(1.5kg)	21(1.0kg)	21(1.5kg)	Qualified product(1.0kg): $\geq 6^{e}$ , $\geq 15^{g}$ ; Premium product(1.0kg): $\geq 12^{h}$
Bentsen air permeance µm/(Pa⋅s)	31.77	2.52	25.43	2.47	Premium product: $\leq 3.2^{a}$ ; prime article: $\geq 2.0^{f}$ ; Qualified product: 0.20 to $6.0^{i}$
Note: a.GB/T 1911 (2011), b.GB/T 1914 (2017), c.GB/T 8938 (2008), d.GB/T 13023 (2008), e.GB/T 13024 (2016), f.GB/T 19341 (2015), g.GB/T 26705 (2011), h.GB/T 30130 (2013), i.GB/T 35594 (2017).					

**Table 1.** Comparison of Paper Properties of Unbleached Pulp and Bleached Pulp

 by Single-cooked and Cycle-cooked with National Standards

The physical properties of the test paper were compared with the national standard, and the results are shown in Table 1. The physical properties of single-cooked and cycle-cooked unbleached pulp paper were able to meet the requirements of GB/T 1914(2017), GB/T 8938(2008), GB/T 19341(2015), GB/T 26705(2011), and GB/T 30130(2013). The physical properties of bleached pulp paper with single-cooked and cycle-cooked procedures were able to meet the requirements of the above national standards, but also meet the requirements of GB/T 1911(2011) and GB/T 35594(2017); however, the physical properties of the unbleached pulp papers prepared by single-cooked and

cycle-cooked did not meet burst index requirements of GB/T 13023(2008) and GB/T 13024(2016).

# Reaction Mechanisms of Preparation of Pulp by Cyclic Cooking with Pulping Spent Liquor Treated by Lime

The lignin degradation reactions: In the early stages of the cooking reaction, under a higher concentration of sodium hydrate, the lignin containing in the lignin-cellulose in wood chips degraded by hydrolytic reaction. And thereby, pulp of cellulose is obtained, at the same time, generating the cooking wastewater called black liquor, which contains the organic substances of lignin-sodium and sugar, as shown as Eq. 2:

 $Lignin - cellulose + NaOH \rightarrow Cellulose + Lignin - Na + Sugar + H_2O$ (2)

Further reactions are proposed to take place in the process of treated black liquor by lime: The cooking wastewater called black liquor were treated by lime to remove of most of the lignin substance by calcified reaction, which reaction generated lignin-calcium precipitate and seldom hydrate. And thereby, successfully recovered a small part of sodium hydrate for wood cooking for pulp, expressed as Eqs. 3, and 4.

$$Lignin - Na_2 + Ca(OH)_2 \rightarrow Lignin - Ca \downarrow + 2NaOH$$
(3)

$$2Resinate - Na + Ca(OH)_2 \rightarrow Resinate_2 - Ca \downarrow + 2NaOH$$
(4)

Based on the reaction mechanisms mentioned above, the increase of pulp yield by recycle cooking with pulping wastewater treated by lime might be increased by the repolymerization reactions between the generated cellulose and the small molecular substances of lignin and sugars containing in the reaction system. Therefore, the reaction mechanisms further identify the feasibility of pulping by recycle cooking with its wastewater.

#### Advantages and Disadvantages of Cyclic-Cooked Method

In summary, chemical pulping of GBG was successfully prepared by cyclic-cooked method, which pulping method increased the pulp yield significantly. The average yield of cyclic-cooked method pulp was 48.6%, being 4.1% greater than the average yield of 44.5% obtained by the ordinary caustic soda method. Moreover, the paper properties of the resulting pulp did not decrease significantly compared with that of the usual single-cooked method. The product still met the requirements of national standards of many kinds of paper. Therefore, this research widens the raw materials for pulp and paper industry.

In addition, the reason for the increase in the pulp yield was analyzed, and the reaction mechanisms of pulping by cycle cooking method were discussed. And thereby, this research enriches the scientific theories in the field of pulping and paper making.

However, there are some shortcomings of the cyclic cooking pulping method. For instance, it was found that the generated pulp is not suitable for bleached pulp, due to it consuming more oxidizing agent to reach the required brightness. In addition, after recycle cooking five times, the quality of pulp was decreased, which was attributed to the accumulation of inorganic salts. Hence, it also needs an evaporator to concentrate a part of the pulping wastewater for combustion for recovery of the sodium hydrate. That traditional alkali recovery process includes 4 steps of concentrated black liquor, combustion of the strong black liquor to generate heat and sodium carbonate, and the sodium carbonate was alkalified by lime to recover sodium hydroxide.

#### CONCLUSIONS

By experiment and analysis, the following conclusions can be obtained:

- 1. The average yield of the cyclic-cooked method pulp was 48.6%, being 4.12% greater than the average yield of 44.5% by the ordinary caustic soda method. The paper properties of the pulp by cyclic-cooked method did not decrease significantly compared with that of the usual single-cooked method. The requirements for many national standards of paper were met.
- 2. The pulp generated by the cyclic-cooking method can be bleached. However, the generated pulp is not suitable for bleached pulp, due to it consuming more oxidizing agent to reach the required brightness.
- 3. Therefore, this research demonstrates that the fast-growing plant of GBG is a good raw material for pulp, and the innovative method of cycle-cooking method can significantly increase the pulp yield.

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