Feasibility of Recycling the Filtrate from Acidified Black Liquor for Alkaline Pulping of Golden Bamboo Grass

Jin-hui Wang,[a] Tian Zhu,[b,c] Yi-jing Li,[b,c] Qian Wang,[a] Yi-kai Ling,[a] Meng-meng Chen,[a] and Guang-zai Nong [a,b,c,*]

To reduce energy consumption, a new pulping process called A-D-E-RC (acidification/desalination/electrolysis/recycle-cooking) was developed by a research group in Guangxi University of China. The present work focuses on the step of recycle cooking (RC) to further investigate the technical feasibility of A-D-E-RC methods. Golden bamboo grass was considered as fiber source material for pulp, and it was cooked with the acidic treating of wastewater from black liquor. Then, the pulp obtained from each cooking was made into paper to test the changes in its physical properties. As a result, the pulp yield increased from 43.9% to 50.2%, after re-using acidified black liquor, and the paper's tear index and tensile index were improved. Therefore, this study demonstrated the feasibility of recycle cooking (RC) fiber materials for pulp applied the acidic treating wastewater from black liquor, and thereby, it further identifies the technical feasibility of A-D-E-RC pulping methods.

DOI: 10.15376/biores.19.3.6160-6177

Keywords: Black liquor; Fiber materials; Filtrate; Pulp; Recirculation

*Contact information: a: College of Resources, Environment and Materials, Guangxi University, Nanning, Guangxi 530004, PR China; b: College of Light Industry and Food Engineering, Guangxi University, Nanning, Guangxi 530004, PR China; c: Guangxi Key Laboratory of Clean Pulp and Papermaking and Pollution Control, PR China; *Corresponding author: gz.nonginguilin@163.com*

INTRODUCTION

Paper plays a significant role in human society, not only as a carrier of information but also as an indispensable material for industries such as packing material for transport of finished goods, which is closely linked to industrial and agricultural production (Sharma *et al.* 2020). The growth of population and economic development will certainly increase the demand for various forest products, leading to a rise in the need for raw materials in the paper industry (Sutradhar *et al.* 2018). The widespread use of computer technology increases paper use, especially for printing and communication (Jiménez *et al.* 2008). Additionally, the surge in online shopping, with platforms like Amazon and Alibaba dominating the market, has heightened the demand for product packaging materials (FAO, 2001). As a result, most pulp and paper enterprises in China and elsewhere have a shortage of lignocellulosic fiber for pulp and paper production (Nong *et al.* 2020). Therefore, actively developing technology to improve pulp yield has continued to be a research focus and hotspot.

Bagasse is India's most abundant agricultural waste. Bhardwaj *et al*. (2019) used caustic soda to cook bagasse, and the pulp yield of bagasse was 46.2%. The highest pulp yield of 32% was achieved by cooking corn stalks at 16% alkalinity at 160 °C for 60 min (Chesca *et al.* 2018). For sunflower pulping with caustic soda, the pulp yield was 37 to

44% due to its different species (Khristova *et al.* 1998). Rodriguez *et al*. (2008) investigated the impact of caustic soda method on the pulp yield of straw, and the highest yield of 35.3% was obtained at a sodium hydroxide concentration of 15 wt%, a reaction temperature of 180 °C, and a reaction time of 90 min. Chibudike *et al.* (2020) reported that pulp yield of 42.6% for bamboo using the caustic soda method (20% NaOH, 160 ºC pulping temperature, 120 min). The above experiments show that the pulp yield using the traditional method is low, necessitating the exploration of new methods to enhance pulp yield.

To protect the earth's environment and safeguard the survival and development of human beings, based on the chemical reaction theory and the characteristics of alkaline pulping, it is proposed to create a new process of waste liquid recycling pulping by the A-D-E-RC method through experimental exploration. The A-D-E-RC recycling process consists of the following four stages: acidification of black liquor with hydrochloric acid for lignin extraction and salt generation (A), Freezing crystallization desalination (D), regeneration of sodium hydroxide and hydrochloric acid by electrolysis of salt (E), and recycling of acidification wastes for cooking of wood chips (RC). Compared with the traditional alkaline pulping method, this method reduces the four links of black liquor concentration, black liquor combustion, lime method green liquor alkali recovery, and lime regeneration; thus, it will significantly reduce the energy consumption and carbon dioxide emission of the pulping process. Figure 1 shows the process of the A-D-E-RC technical method.

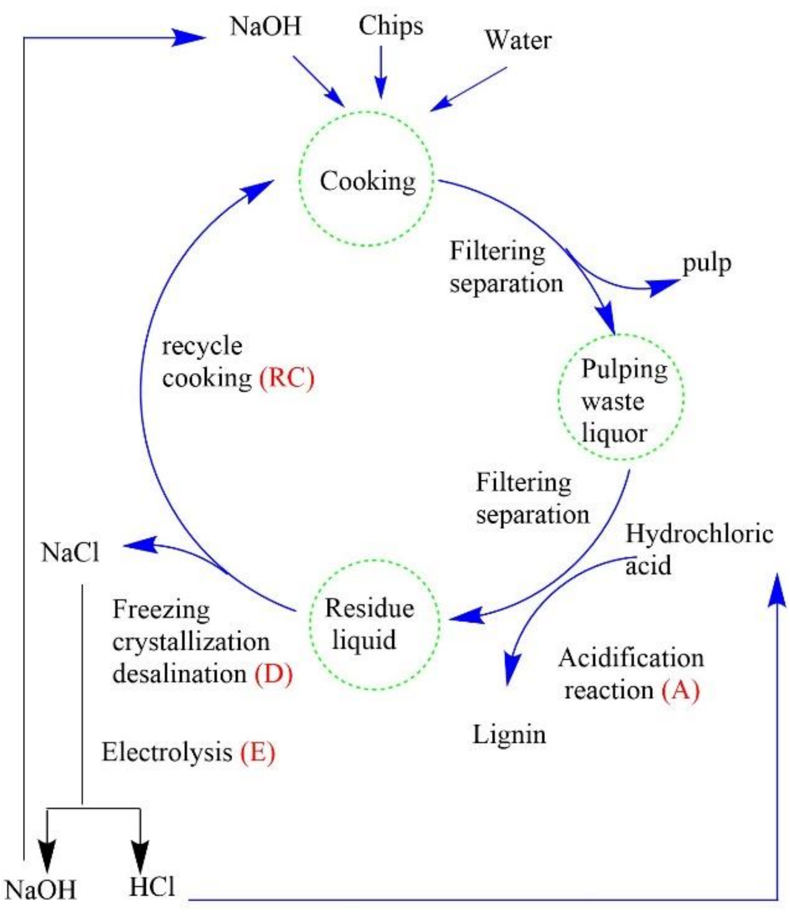

Fig. 1. The process of A-D-E-RC technical method

Black liquor is the liquid generated during alkali pulping (Al-Kaabi *et al.* 2019), containing a large amount of organic matter primarily composed of lignin, hemicellulose, fine fibers, sugar molecules (Cardoso *et al.* 2009), and other substances, and it can be considered as a renewable resource (Li *et al.* 2021). However, if discharged directly without treatment, it can cause massive pollution to the natural environment (Yang *et al.* 2010). Lignin can be removed from the black liquor after acidification, so the remaining acidified filtrate contains a large amount of fine fibers and dissolved sugar molecules.

In conjunction with previous studies (Li *et al.* 2023), this paper focuses on the recycle cooking (RC) step. The black liquor from the hydrochloric acid treatment is used to prepare chemical pulp by recirculation cooking, using golden bamboo grass as pulp fiber source material. In this work, hydrochloric acid was used to treat the black liquor directly, and the acidified filtrate obtained after removing most of the lignin contained some organic matter. The lignin from the pulping liquid can be returned to the fibers, thus increasing the pulping yield. Then, the changes in the physical properties of the generated pulp were tested and it was found that the tear index and tensile index of the paper were improved (Bose et al. 1999). Therefore, this experiment has the potential to show that recycle cooking (RC) for the pulping of fiber material is a high-quality method, and the technical feasibility of the A-D-E-RC pulping method can be further speculated.

EXPERIMENTAL

Materials

Golden bamboo grass (with a growth period of 3 months, reaching a plant height of approximately 2.8 meters, culm diameter ranging from 1.5 to 2.0 cm, and wall thickness about 0.3 cm) is a perennial crop without pollen seeds, cultivated only by biological breeding; it is vigorous, rough, and easy to grow and has a wide range of soil adaptability (drought, flood, cold, lean, and saline tolerant), resistance to pests and diseases, and high yield. In addition, it has a high cellulose content, a low lignin content, and a good fiber form, which makes it an excellent raw material for pulp and paper production. For these reasons, golden bamboo grass was selected as a fiber raw material.

The golden bamboo grass was cut into strips with an average length of 2.5 to 3.0 cm and a width of 1.0 cm. These strips were placed outdoors to air dry before being gathered and stored in plastic sealed bags to equilibrate moisture. The moisture content of strips was determined. Subsequently, the dried strips were utilized as raw materials for the cooking experiments.

Pulping of Golden Bamboo Grass by Caustic Soda Method

First, 50 g of dried golden bamboo grass, sodium hydroxide and water were added to a rotary pulping cooker. The charge of sodium hydroxide was 20% of the total mass of dried golden bamboo grass, and the mass ratio of dried golden bamboo grass to water was 1:6. The conditions for cooking golden bamboo grass were to heat it for 2 h to raise the temperature in the cooker from room temperature to 165 °C and to keep it at 165 °C for 2 h. The rotary pulping cooker was heated while maintaining a proper rotational speed so that the golden bamboo grass and the cooking liquid were fully mixed and impregnated. After cooking, the pulp and black liquor were drained and separated. The pulp obtained by cooking was continuously washed using a slurry bag until the washing solution became clear; then, the pulp was shaken dry and torn and finally stored in a sealed bag and put into a refrigerator for storage to equilibrate moisture content of the pulp.

Acidification of Black Liquor with Hydrochloric Acid

The acidification reaction of black liquor produced acidified filtrate and lignin. Hydrochloric acid at a concentration of 37% was added with constant stirring to bring the pH of the black liquor to 7, which led to the precipitation of some of the lignin. Lignin was separated by filtration to obtain the filtrate of acidified black liquor (Mendes *et al.* 2022). The lignin separated by this process can be used as a raw material for the production of dyes, fertilizers and other products, adding economic value to the process.

Pulping of Golden Bamboo Grass Using the Acidified Filtrate from Black Liquor

Sodium hydroxide, 50 g of dried golden bamboo grass, water, and the filtrate from the acidified black liquor were added to the rotary pulping cooker for cooking; the mass ratio of dried golden bamboo grass to cooking liquor was 1:6. The charge of sodium hydroxide was 20% of the total mass of dried golden bamboo grass. Compared with the caustic soda method, the acidified filtrate replaced 40% to 50% of the water in the cooking of golden bamboo grass, and the alkalinity of the cooking solution did not change much due to the neutrality of the acidified filtrate. The golden bamboo grass was heated for 2 h to raise the temperature in the cooker from room temperature to 165 °C and to keep it at 165 °C for 2 h. The rotary pulping cooker was heated while maintaining a proper rotational speed so that the golden bamboo grass and the cooking liquid were fully mixed and impregnated. After cooking, the pulp and black liquor were drained and separated. The pulp obtained by cooking was continuously washed using a slurry bag until the washing solution became clear; then, the pulp was spin- dried and torn and finally stored in a sealed bag and put into a refrigerator for storage to equilibrate moisture content of the pulp. The black liquor was acidified, and the separated filtrate, after precipitation of some of the lignin, could then be used for the next cooking.

Bleached Pulp

The pulp was placed in a refrigerator for one day to equilibrate the moisture, which was measured and recorded. A total of 10 g of dried pulp was put into a polyethylene-sealed bag, and then water, dilute sulfuric acid of pH=1, and 30% concentration of chlorine dioxide solution were added so that the pulp concentration was 10%, the pH value was 2, and the dosage of chlorine dioxide was 1 to 6% of the weight of dry pulp. Then, polyethylene-sealed bags were placed into the constant temperature water bath at a constant temperature of 70 °C, bleaching for 1.5 h (Nong *et al.* 2019). At the end of bleaching, the pulp was removed and loaded into non-woven pulp bags for complete washing. The brightness of the bleached pulp was measured according to the TAPPI Test Method, and the pulp kappa value test method was referred to GB/T 1546-2018 for testing.

Analysis of Pulp Structure and Composition

Electron microscope

The conventional soda pulping and soda pulping with addition of filtrate from the acidified black liquor were placed in a vacuum drying box and dried at 50 °C for 48 h. The pulp was separately torn with tweezers into long and wide sheets of 2 mm and sprayed with gold. The pulp was photographed using a sigma 300 scanning electron microscope from Carl Zeiss Management GmbH, Germany, to observe the morphological characteristics of the pulp.

FTIR

The conventional soda pulping and soda pulping with addition of acidified black liquor were placed in a vacuum drying box and dried at 50 °C for 48 h. The pulp was torn into slices about 1 cm long and wide. Pulp was tested in the wavenumber range of 400 to 4000 cm^{-1} using the Fourier Transform Infrared Spectrometer (Nicolet iS 50) from Thermo Fisher, USA.

XPS

The pulp of approximately 2 mm in length and width was attached to the sample stage, which was placed into a Thermo Scientific K-Alpha XPS instrument in the United States, and fed the sample into the analysis chamber when the pressure in the sample chamber was less than 2.0×10^{-7} mbar, with a spot size of 400 μm. The operating voltage was 12 kV, and the filament current was 6 mA; the full-spectrum scanning fluence energy was 150 eV with a step size of 1 eV; and the narrow-spectrum scanning fluence energy was 50 eV with a step size of 0.1e V.

Pulp composition test

The pulp was examined using Van Soest's washed fiber analysis (Naeini *et al.* 2014).

Handsheet Formation and Paper Performance Testing

Stock dilution

The paper's basis weight was 80 g/m^2 and the paper area was 314 cm^2. A total of 2.512 g of dry pulp was transferred to the dilution pool, diluted with water, and stirred to form a homogeneous low-consistency pulp of 2 to 5%.

Beating

The low-consistency pulp was beaten using the pulp beater (AG04) produced by Estanit Company, Germany. The beating degree of the pulp was tested at different beating times, selecting a beating degree in the range of 33 to 37 °SR. After beating, the pulp was transferred to the pulp pool.

Papermaking

Kaiser-type sheet formers (BB type) produced by Ernst Haage Company, Germany were used to produce the corresponding paper products.

Paper performance testing

To test the performance of the paper, various equipment was used, including the TMI 83-20 Tear Tester, L&W Tensile Tester, and TMI EC3x Burst Tester. These tests were conducted in accordance with international standards such as GB/T 12914-2018, GB/T 455-2002, and GB/T 454-2020.

Black Liquid Composition Analysis

Measurement of solids

First, 3 mL of black liquor was placed in a clean bottle and dried at 100 to 110 ℃ for 8 h. After drying, the sample was placed at room temperature to cool. It was weighed accurately and then dried until the sample reached a constant weight.

Measurement of organic and inorganic substances

Dry black liquid solid was placed in a crucible in an electric convection drying oven in constant temperature drying and then transferred to a muffle furnace at 800 ℃ burning to constant weight. After weighing the solid residue, the mass of the organic matter was calculated to get the percentage of the content of each substance.

Measurement of SiO_2 content in black liquor

A total of 10 g of absolute black liquor solid was burned. The molten substance was cooled, dissolved in 500 mL of deionized water, and filtered to get clear green liquid. Next, 5 mL of clear green liquid was titrated with 1 M hydrochloric acid until it reached pH 5.0. After the titration, the filter was filtered by quantitative filter paper and washed with deionized water. The filter residue was placed in muffle furnace and burned to constant weight at 850 ℃. After cooling, the SiO_2 mass was obtained by weighing (Yuan *et al.* 2018).

Chemical oxygen demand (COD)

First, 1 mL of black liquor was diluted to 20 mL in a 250-mL reflux conical flask, and 10 mL of potassium dichromate standard solution was added. After heating reflux, the organic matter in the diluted black liquor was oxidized. After cooling, 3 drops of ferroin indicator solution were added, and the sample was titrated with ferrous ammonium sulfate standard solution, according to the amount of potassium dichromate standard solution consumed to calculate the chemical oxygen demand. Reagent concentrations were standard solution (Graner *et al.* 1998).

RESULTS AND DISCUSSION

Pulp Yield by Caustic Soda and Cyclic Cooking

In Fig. 2, the filtrate of the acidified black liquor was re-used five times and after each cook, the black liquor was acidified and the filtrate was re-used after precipitating a portion of the lignin. Three cookers were used for each cooking, and the pulp yield was calculated separately, and the error bars of the pulp yield for each cooking are shown in Fig. 2. The pulp yield from the recirculation of filtrate from the acidified black liquor for cooking of golden bamboo grass increased with the number of cooking cycles. However, the increase gradually decreased, and the pulp yield was almost the same for the fourth and fifth cooking cycles. The pulp yield of the first cycle cooking was 46.27%, the pulp yield of the fifth cycle cooking was 50.16%, and the pulp yield ranges from 46.27% to 50.16%. Compared with the caustic soda pulping process, the pulping yield increased by 6.26%. The results suggest that the recirculation cooking of filtrate of the acidified black liquor enhances pulp yield during the pulping process.

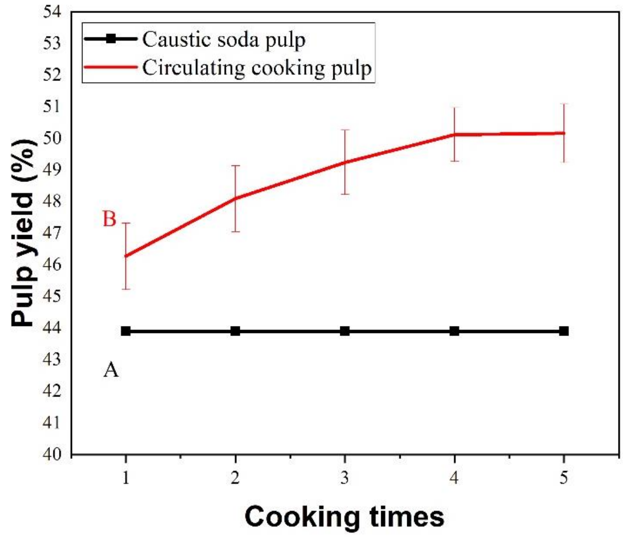

Fig. 2. Relationship between cooking times and pulp yield

Bleaching Results

Figure 3 shows the relationship between brightness, Kappa number, and chlorine dioxide dosage. At 70 °C, pH=2, and a bleaching time of 90 min, the average brightness increased faster at chlorine dioxide dosages in the range of 1.0 to 5.0%. At 5 to 6.0%, the increasing trend of brightness became slow. In short, the average brightness of paper increased with chlorine dioxide. At 6.0% chlorine dioxide dosage of crude pulp, the average brightness of the fibers was 57.1% ISO, and the yield was 91.6% relative to the initial fiber mass. The Kappa numbers decrease as the dosage of chlorine dioxide increases, and the Kappa numbers do not change much after the dosage of chlorine dioxide reaches 5%. The results show that for single-stage bleaching, the best bleaching effect has been achieved at a chlorine dioxide dosage of 6%, and this condition was used to bleach the circulating cooking pulp, and the bleaching results are shown in Fig. 4.

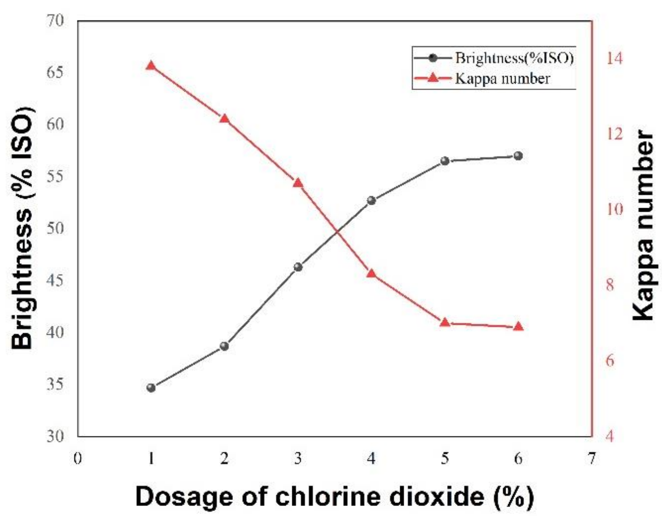

Fig. 3. Relationship between brightness, Kappa number, and dosage of chlorine dioxide

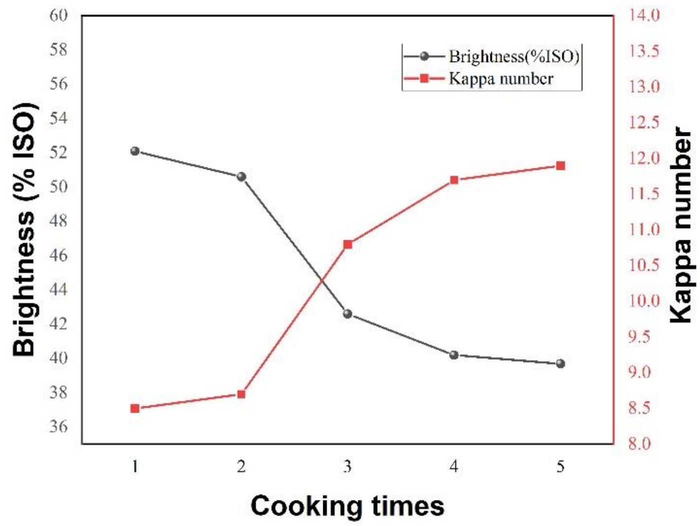

Fig. 4. Relationship between brightness, Kappa number, and cooking times

Figure 4 shows the relationship between the brightness, kappa number, and cooking times for single-stage bleaching of pulp under the same bleaching conditions. After single-stage bleaching, the brightness of the soda pulping with addition of filtrate from the acidified black liquor was lower than that of the conventional soda pulping, and as the number of cooking times increased, the brightness gradually decreased and the Kappa number gradually increased. This indicates that as the cooking times increases, the bleaching efficiency decreases due to the gradual rise in non-cellulosic material content. Consequently, the use of filtrate from acidified black liquor for cooking adds difficulty to pulp bleaching.

Black liquor ingredients

The performance indexes of black liquor are shown in Table 1, in which the first group is black liquor cooked by caustic soda method, and the 2nd to 6th are the results of 5 times cycle cooking black liquor. From the results, it can be seen that, with the increase of the number of cycle cooking, the solids content after cooking showed a rising trend, SiO_2. Inorganic matter first rose and then fell and then showed a rising trend. Organic matter and COD first rose and then tended to stabilize. Among them, the performance of black liquor after cyclic cooking was higher than that of black liquor cooked by caustic soda method.

Table 1. Black Liquor Alternative Cooking Black Liquor Performance Indexes

	Solid Content (%)	COD (mg/L)	SiO_2 Content (g/L)	Organic Compound (g/L)	Inorganic Compound (g/L)
1	10.3	108133	4.28	88.3	44.32
2	13.2	10853	4.67	92.7	48.16
3	12.7	10503	4.74	93.6	53.27
4	13.6	110033	4.46	94.4	50.46
5	13.4	109833	4.68	97.9	54.84
6	13.7	113500	4.93	102.6	56.85

With the increase in the number of cycle cooking, the SiO_2 content was higher than the original black liquor, but in the fourth group of black liquor silica content decreased, indicating that deposition of SiO_2 in the pulp, but no longer a threat to the circulatory system; solid content, organic content and COD have increased, but the rate of increase is constantly decreasing, indicating that with the cooking, lignin and other organic matter is constantly dissolved, and ultimately reached equilibrium.

Acidified black liquor ingredients

Table 2 shows that after hydrochloric acid acidification, there was little change in the inorganic matter, but there was a great decrease in the solids content, SiO_2 content, COD, and organic matter content of the black liquor. The reaction of hydrochloric acid with black liquor results in the precipitation of lignin, which is the primary cause of the reduction in solid content, organic matter content, and COD of the acidified filtrate. Additionally, hydrochloric acid reacts with SiO_2 to form silicate precipitation, leading to a decrease in SiO_2 content and viscosity of the acidified filtrate (Minu *et al.* 2012). This reduction in viscosity is advantageous for subsequent cooking processes. Furthermore, the concentration of dissolved lignin and hemicellulose in the acidified black liquor filtrate is likely the main factor contributing to the increased pulp yield observed (Jahan *et al.* 2004).

Table 2. Comparison of Acidulated Black Liquid Ingredients

	Solid Content (%)	Cod (Mg/L)	SiO_2 Content (G/L)	Organic Compound (G/L)	Inorganic Compound (G/L)
Black Liquor	10.3	108133	4.28	88.3	44.32
Acidified Black Liquor	4.2	73833	1.16	36.7	43.9

Electron Microscopy

In Fig. 5, the left panel shows an electron microscope image of the pulp after cooking by the caustic soda method; the right image shows the electron microscope image of the pulp after the fifth cyclic cooking. According to Fig. 5, it can be seen that after the cyclic cooking, the voids between the fibers were reduced, and the interweaving was increased. There was a large amount of spherical particle adhesion after vacuum drying. It can be inferred that these spherical particles consisted mainly of lignin, which adhered to the cellulose surface during cyclic cooking.

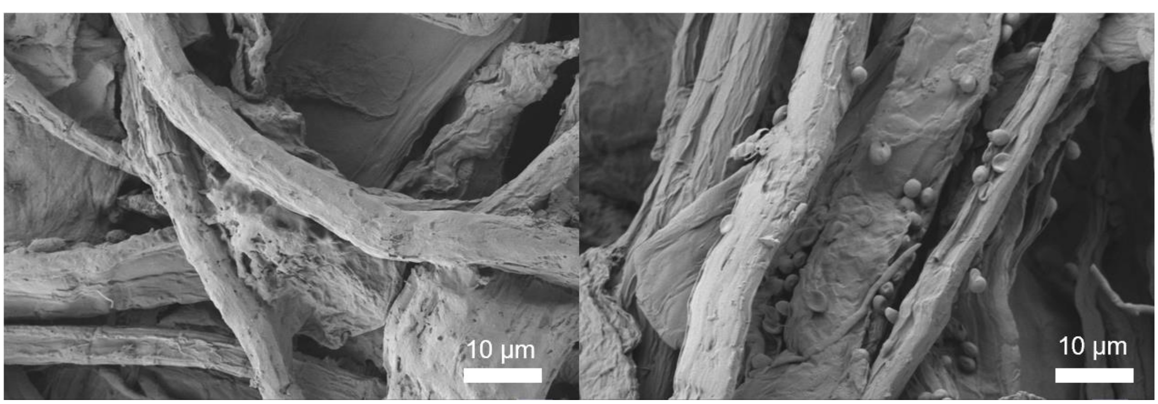

Fig. 5. Electron micrographs of pulp before and after recirculation cooking of acidified filtrate

FTIR

FTIR spectroscopy is used to analyze the change of functional groups in the recirculating cooking pulp, compared with the un-recirculating cooking pulp. The functional group types of the two pulps were the same, and no new functional groups were observed. The vibration absorbance peak at 3334 cm^{-1} of the cyclic cooking pulp fiber was more robust than that of the caustic soda pulp, indicating that the number of hydrogen bonds between hydroxyl groups increased. The peak at 2885 cm^{-1} represents the stretching vibration of $-CH_2-$. The absorbance peak of cyclic cooking at 1653 cm^{-1} was significantly more substantial than that of caustic soda cooking, which indicates that the carbonyl vibration was stronger after cyclic cooking. The benzene ring and the phenol vibrate the absorption peaks at 1521 and 1331 cm^{-1}; this indicates that after recycling, the lignin content of the pulp was elevated. The peak at 1033 cm^{-1} of the cycle-cooked pulp represents a vibrational contraction of the C-OH of the sugars (Strunk *et al.* 2011).

The enhancement of these absorption peaks after cyclic cooking confirms that cyclic cooking increases the amount of aromatics and polysaccharides mixed into the pulp. Thus, it can be demonstrated that some small molecular weight lignin binds to cellulose.

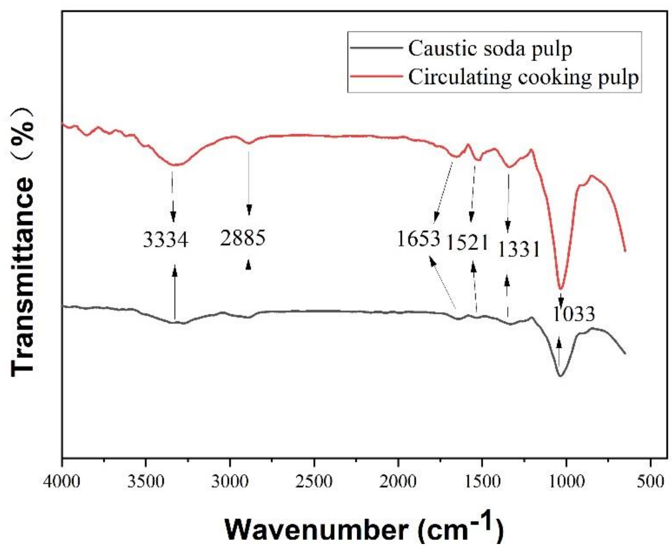

Fig. 6. FTIR spectra of pulp

XPS

Figures 7(a) and (b) show the XPS survey and C1s scan of the first cooking pulp, while (c) and (d) show the XPS survey and C1s scan of the recycled cooking pulp. In (b) and (d), C1 stands for C-H, C-C, C2 represents C-O, and C3 stands for O-C-O, C=O (Deng *et al.* 2008). The data from Fig. 7 is represented in Table 3.

The oxygen content on the surface of the pulp increased after cyclic cooking, and the value of O/C increased from 29.0% to 41.2%. This result indicates that the lignin content of the pulp surface was enhanced after acidified filtrate recirculation cooking. (Gustafsson *et al.* 2003). Comparing Fig. 7(b) and (d), C2 and C3 increased after cyclic cooking. Thus, during the cooking cycle, the pulp undergoes a condensation reaction on the surface, producing a large amount of C=O. Combined with the FTIR spectroscopy, the results indicated that cellulose and small molecule lignin reacted during the cooking process.

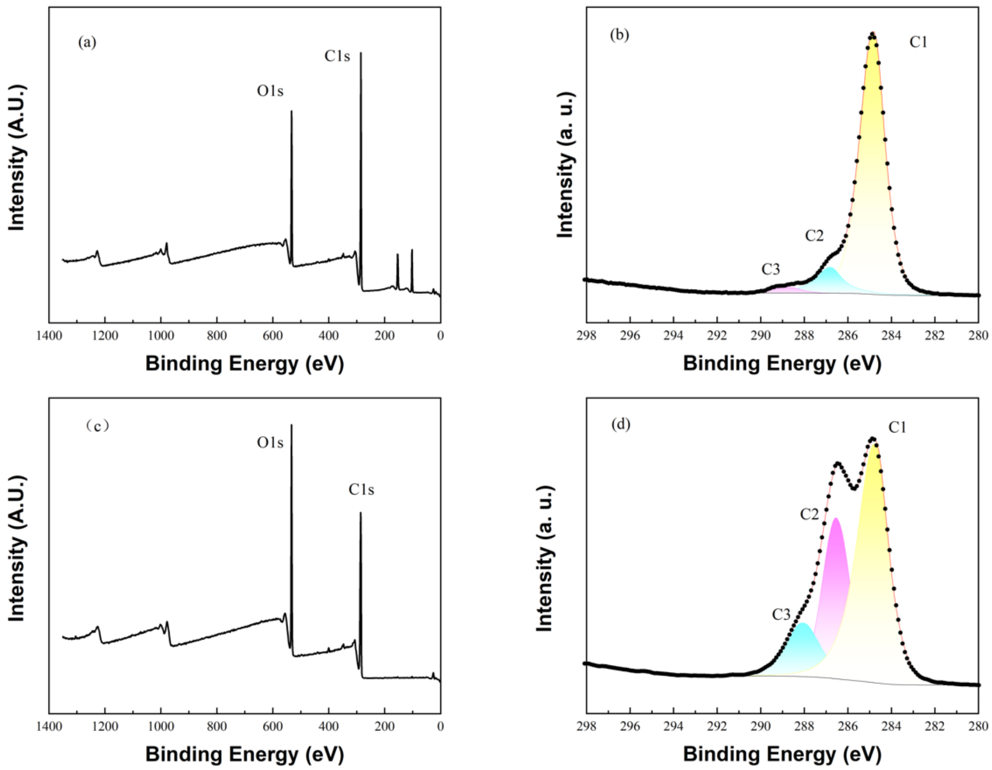

Fig. 7. XPS survey and C1s scan of pulp

Table 3. Values of O/C Ratio and Individual Peaks of C1s on Pulp Surface Before and After Cyclic Cooking

	O/C	C1	C2	C3
First cooking pulp	29.02%	86.89%	11.14%	1.97%
Recycled cooking pulp	41.24%	56.55%	29.23%	13.52%

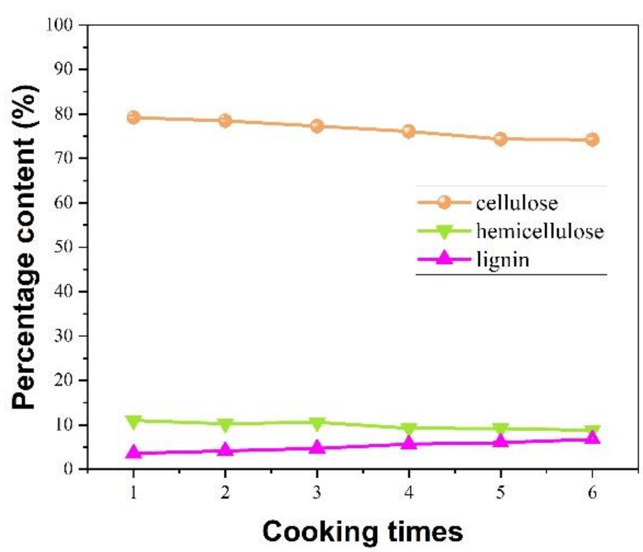

Fig. 8. Percentage of cellulose, hemicellulose and lignin in pulp

Pulp Composition Test

In the testing process, it is necessary to wash off the sugar, starch, fat, and other soluble substances. For that reason, the measured content sum is not 100% (see Fig. 8). The first of these cooking operations was done just with caustic soda, whereas the cooking times numbered from 2 to 6 times involved cycle cooking using acidified filtrate. The data presented in the figure shows that as the cooking times increased, the cellulose content in the pulp gradually decreased from 79.3% to stabilize at 74.3%, whereas hemicellulose content decreased from 10.8% to stabilize at 9%, and lignin content increased from 3.6% to stabilize at 6.7%. This suggests that the lignin content of the pulp increased as the cooking times increase, eventually reaching a dynamic equilibrium. This explains the increase in pulp yield.

Freeness Development of the Pulps

The effect of different number of cycles of cooking on the pulping performance of pulp with different cycles of cooking is shown in Fig. 9 for the pulping treatment with PFI mill. In Fig. 9, the first cooking corresponds to the caustic soda method, and the second to sixth times are with the acidified filtrate cycle cooking.

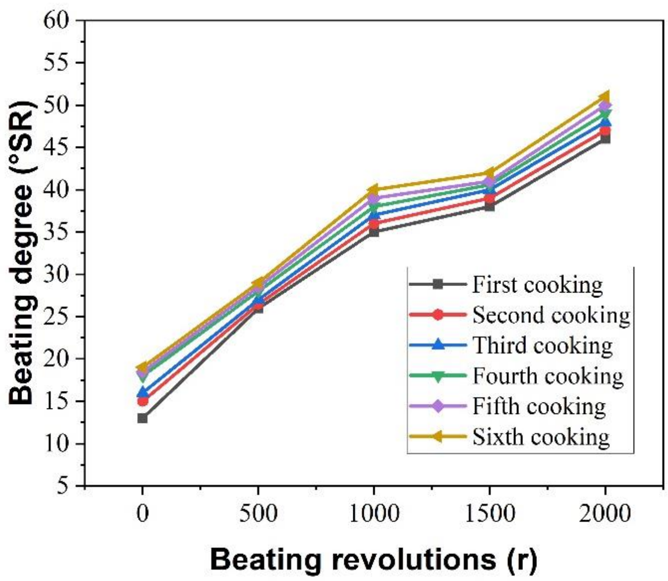

Fig. 9. Effect of cyclic cooking on pulp beating performance

The pulping degree of the pulp obtained by the caustic soda method was 14 °SR, and the pulping degree was 46 °SR after 2000 r. In the course of continuing to increase the number of circulating cooking times to the sixth time, the pulping degree of the untreated pulp was 19 °SR, and the refining degree of the pulp was 51 °SR after 2000 r. The refining degree of the pulp obtained from different cycle cooking times all increased with the increase in the number of pulping revolutions. This was attributed mainly to the fact that with the pulping treatment, the golden bamboo grass pulp fibers are subjected to the action of shear force, which produces the effect of fiber water absorption and expansion and the phenomenon of fine fibrillation (Shao *et al.* 2017). At the same number of pulping revolutions, the pulping degree of pulp fibers increased slightly with the increase in the number of circulating cooking, which indicates that the acidified filtrate used for circulating cooking of the pulp obtained from golden bamboo grass is easy to pulp, and it could reduce the pulping energy consumption of the PFI pulper. Acidified filtrate liquid contains more degradation products. These degradation products will be deposited on the pulp, resulting in a lot of fine fiber components, the pulp filtration water decreases, and thus it is easy to beat the pulp (Liu *et al.* 2008).

Mechanical Properties of the pulps

Cyclic cooking pulp was treated under the same conditions as caustic soda pulp. Tearing index, burst index, tensile index, breaking length, and their relationship with the number of cooking times are shown in Fig. 10. Figure 10(a) shows the physical properties of caustic soda-cooked golden bamboo grass pulp, and Fig. 10(b) shows the physical properties of acidified filtrate-cooked golden bamboo grass pulp.

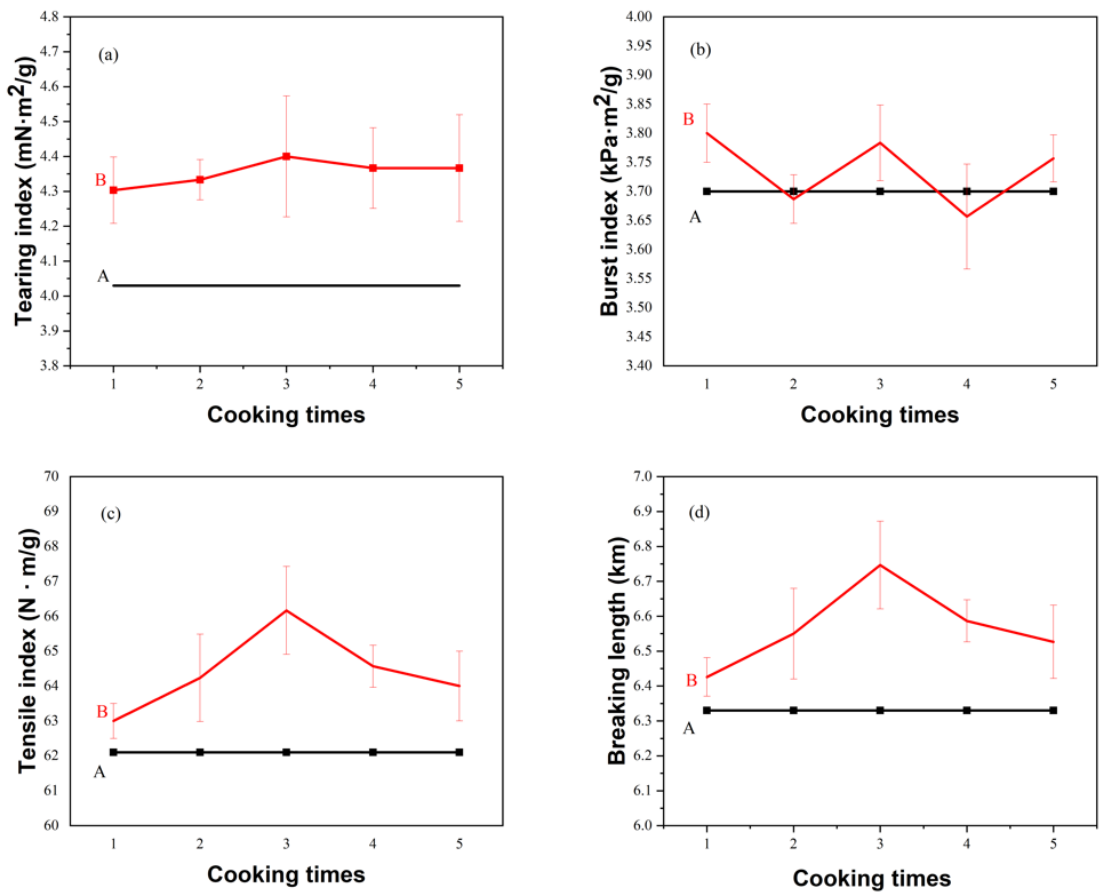

Fig. 10. Relationship between the number of cooking times and the physical properties of the paper

Figure 10(a) shows the relationship between the number of cooking cycles and the pulp's tearing index. In comparison, the tear index of initial cycle cooking pulp was 4.3 mN·m^2/g, and the tear index of multiple cycle cooking was higher than that of conventional caustic soda. The tear index of acidified filtrate cycle cooking pulp was significantly higher than that of conventional caustic soda method pulp.

Figure 10(b) shows the relationship between the number of cooking cycles and the burst index. The burst index of the first acidified filtrate cooking pulp was 3.8 kPa·m^2/g. In contrast, the burst index of the recycled cooking pulp remained stable in the range of 3.65 to 3.8 kPa·m^2/g; the bursting index was not much different from that of the conventional caustic soda method.

Figure 10(c) shows the relationship between the number of cycles and the tensile index of the pulp. The tensile indices of the cycle-cooked pulps fluctuated slightly with the number of cooking times, but all exceeding the tensile index of 62.1 N·m/g for the caustic soda-cooked pulps.

Figure 10(d) shows the relationship between the number of cycles and the breaking length of the pulp. With the increase in cycles, the breaking length first increased and then decreased, and the highest breaking length was 66 km in the third cycle of cooking pulp. All exceeded the 6.33 km breaking length of the caustic soda pulp.

A comparison shows that after cyclic cooking, the tensile index and tear index of the paper had been improved, and the breakage index had not been reduced, which indicates that cyclic cooking had a beneficial effect on the performance of the paper.

Table 4. Comparison of Pulp Properties Before and After Bleaching

	Tearing index (mN·m^2/g)	Burst index (kPa·m^2/g)	Tensile index (N·m/g)	Breaking length (km)
Unbleached pulp	4.4	3.78	66.1	6.74
Bleached pulp	4.52	3.85	66.4	6.775

Table 4 shows the comparison of pulp properties before and after the third cycle of cooking pulp bleaching, and it can be found that the physical properties of pulp were slightly improved after pulp bleaching, and the bleaching can remove part of the lignin in the pulp so that the properties of pulp were improved.

Reaction Mechanism of Acidified Black Liquor Filtrate Circulating Cooking Pulping

In the early stages of the cooking reaction, in the presence of higher concentrations of sodium hydroxide, the lignin in golden bamboo grass was degraded by a hydrolysis reaction. This resulted in pulp, while a black liquor containing lignin-sodium and sugar was produced. The black liquor was acidified and filtered, and the filtrate was reused for cooking. This process removes most of the lignin through the acidification reaction, so that the recovered filtrate could be used to cook the golden bamboo grass, after addition of alkali. Based on the above reaction mechanisms, the increase in pulp yield from recycled cooking of hydrochloric acid-treated pulping wastewater may be due to the re-deposition of components from the generated cellulose and the lignin and sugar small molecules contained in the reaction system onto the fibers. Thus, these reaction mechanisms further confirm the feasibility of using cooking wastewater for recycled pulp production.

Discussing Advantages and Disadvantages of this Method

In summary, the chemical pulp was successfully prepared by the recirculation cooking method, which significantly improved the pulp yield. The highest yield of 50.2% of pulp was obtained by the recirculation cooking method, which was 6.26% higher than the average yield of 43.9% obtained by the normal caustic soda method. In addition, the paper properties of the resulting pulp were not significantly reduced compared with those of the usual caustic soda method. This demonstrates the feasibility of acidified filtrate recirculation cooking pulp, thus further indicating the technical feasibility of the A-D-E-RC pulping method. In addition, the reasons for the increase in pulp yield were analysed to enrich the scientific theory in the field of pulp and paper making. (Liang *et al.* 2011).

However, the recirculation cooking method has some drawbacks. For example, the resulting pulp has elevated lignin content and requires more bleach for bleaching than the pulp obtained by the caustic soda method, making it unsuitable for grades of pulp that require bleaching. In addition, this method adds the step of hydrochloric acid acidification and black liquor filtration, which increases the use of chemicals and filtration apparatus.

CONCLUSIONS

1. The maximum yield of pulp by the recirculation cooking method was 50.2%, which was 6.3% higher than the yield of 43.9% when using the ordinary caustic soda method. There was no significant reduction in the paper properties of pulp when using the recirculation cooking method.
2. Pulp produced by the recirculation cooking method had a higher lignin content than that obtained by the caustic soda method and it required the consumption of more oxidising agent to achieve the desired brightness. Therefore, the pulp produced was judged as not suitable for bleaching.
3. Therefore, the present study shows that recirculation cooking can be a superior method of pulping, which greatly affirms the A-D-E-RC method of pulping technology.

ACKNOWLEDGMENTS

This project is supported by the Regional Project of the Natural Science Foundation of China (Grant#.:22368007).

REFERENCES CITED

Al-Kaabi, Z., Pradhan, R., Thevathasan, N., Gordon, A., Chiang, Y. W., and Dutta, A. (2019). "Bio-carbon production by oxidation and hydrothermal carbonization of paper recycling black liquor," *Journal of Cleaner Production* 213, 332-341. DOI: 10.1016/j.jclepro.2018.12.175

Bhardwaj, N. K., Kaur, D., Chaudhry, S., Sharma, M., and Arya, S. (2019). "Approaches for converting sugarcane trash, a promising agro residue, into pulp and paper using soda pulping and elemental chlorine-free bleaching," *Journal of Cleaner Production* 217, 225-233. DOI: 10.1016/j.jclepro.2019.01.223

Bose, S. K., Akhtaruzzaman, A. M. F., and Khan, H. R. (1999). "Effect of spent liquor recirculation on NS-AQ pulping of jute," *TAPPI Journal* 82(5), 148-151.

Cardoso, M., de Oliveira, E. D., and Passos, M. L. (2009). "Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills," *Fuel* 88(4), 756-763. DOI: 10.1016/j.fuel.2008.10.016

Chesca, A. M., Nicu, R., Tofanica, B. M., Puitel, A. C., and Gavrilescu, D. (2018). "Optimization of soda pulping process of corn stalks by response surface modelling," *Cellulose Chemistry and Technology* 52(9-10), 823-831.

Chibudike, H. O., Ndukwe, N. A., Nkemdilim Ifeanyi, O., Adeyoju, O. A., and Chibudike, E. C. (2020). "Soda pulping experiments and yield optimization on bamboo fiber for pulp and paper production," *GSJ* 8(11).

Das, T. K., and Houtman, C. (2004). "Evaluating chemical-, mechanical-, and bio-pulping processes and their sustainability characterization using life-cycle assessment," *Environmental Progress* 23(4), 347-357. DOI: 10.1002/ep.10054

Deng, Y. M., He, B. H., and Qian, L. Y. (2008). "Study on mechanical pulp's fiber surface properties using AFM and XPS," in: *International Conference on Pulping, Papermaking and Biotechnology*, Nanjing Forestry Univ, Nanjing, China.

Food and Agriculture Organization of the United Nations (FAO) (2001). *State of the Worlds Forests 2009*.

GB/T 1546 (2018). "Pulp – Determination of Kappa number," Standardization Administration of China, Beijing, China.

GB/T 12914 (2018). "Paper and board – Determination of tensile properties – Constant rate of elongation method (20 mm/min)," Standardization Administration of China, Beijing, China.

GB/T 454 (2020). "Paper – Determination of bursting strength," Standardization Administration of China, Beijing, China.

GB/T 455 (2002). "Paper and board determination of tearing resistance," Standardization Administration of China, Beijing, China.

Graner, C. A. F., Zuccari, M. L., and de Pinho, S. Z. (1998). "Chemical oxygen demand (COD) determination in waters by simultaneous spectrophotometry of chromium (III) and dichromate ions," *Ecletica Quimica* 23, 31-44. DOI: 10.1590/s0100-46701998000100003

Gustafsson, J., Lehto, J. H., Tienvieri, T., Ciovica, L., and Peltonen, J. (2003). "Surface characteristics of thermomechanical pulps; the influence of defibration temperature and refining," *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 225(1-3), 95-104. DOI: 10.1016/s0927-7757(03)00320-0

Jahan, M. S., Chowdhury, D. A. N., Islam, M. K., and Hossain, S. N. (2004). "Studies on the spent liquor recirculation during soda-amine pulping of jute," *Journal of Scientific and Industrial Research* 63(9), 758-762.

Jiménez, L., Rodríguez, A., Pérez, A., Moral, A., and Serrano, L. (2008). "Alternative raw materials and pulping process using clean technologies," *Industrial Crops and Products*, 28(1), 11-16. DOI: 10.1016/j.indcrop.2007.12.005

Khristova, P., Gabir, S., Bentcheva, S., and Dafalla, S. (1998). "Soda-anthraquinone pulping of sunflower stalks," *Industrial Crops and Products* 9(1), 9-17. DOI: 10.1016/s0926-6690(98)00008-9

Li, H. K., Wu, S. J., Dang, C. X., Yang, G. X., Cao, Y. H., Wang, H. J., Peng, F., and Yu, H. (2021). "Production of high-purity hydrogen from paper recycling black liquor *via* sorption enhanced steam reforming," *Green Energy and Environment* 6(5), 771-779. DOI: 10.1016/j.gee.2020.07.002

Li, Y. J., Zhu, T., Qin, S. J., Nong, G. Z., and Yin, Y. J. (2023). "Energy conservation and emission reduction of a new pulp mill by improving production processes," *Process Safety and Environmental Protection* 176, 662-672. DOI:

10.1016/j.psep.2023.06.027

Liang, J. D., He, Y. L., Zhu, J. W., and Du, W. J. (2011). "Accumulation of dissolved and colloidal substances in water recycled during papermaking," *Chemical Engineering Journal* 168(2), 604-609. DOI: 10.1016/j.cej.2011.01.030

Liu, Y., Wang, Z. J., and Luo, Q. (2008, May 14-16). "Effect of beating on morphology of straw fiber," in: *2nd International Papermaking and Environment Conf.*, Tianjin, China.

Mendes, S. F., Pasquini, D., Cardoso, V. L., and Reis, M. H. M. (2022). "Ultrafiltration process for lignin-lean black liquor treatment at different acid conditions," *Separation Science and Technology* 57(12), 1936-1947. DOI: 10.1080/01496395.2021.2013890

Minu, K., Jiby, K. K., and Kishore, V. V. N. (2012). "Isolation and purification of lignin and silica from the black liquor generated during the production of bioethanol from rice straw," *Biomass and Bioenergy* 39, 210-217. DOI: 10.1016/j.biombioe.2012.01.007

Naeini, S. Z., Emami, N. K., Rowghani, E., and Bayat, A. (2014). "Influence of ensiling time on chemical composition, fermentation characteristics, gas production and protein fractions of sweet sorghum silage," *Research Opinions in Animal and Veterinary Sciences* 4, 286-293.

Nong, G., Li, P., Li, Y., Xing, D., and Yin, Y. (2019). "Preparing tea filter papers with High air permeability from jute fibers for fast leaching," *Industrial Crops and Products* 140, article 111619.

Nong, G. Z., Xing, D. Y., Li, Y. J., Zhu, T., and Li, X. R. (2020). "Recycle cooking wood chips with the residue liquid removed out of lignin by calcification for increasing pulp yield and reducing waste water discharge," *Journal of Cleaner Production* 277, article 124028. DOI: 10.1016/j.jclepro.2020.124028

Rodriguez, A., Moral, A., Serrano, L., Labidi, J., and Jimenez, L. (2008). "Rice straw pulp obtained by using various methods," *Bioresource Technology* 99(8), 2881-2886. DOI: 10.1016/j.biortech.2007.06.003

Shao, S. C., Wu, C. Z., and Chen, K. L. (2017). "Refining, dewatering, and paper properties of soda-anthraquinone (Soda/AQ) pulp from rice straw," *BioResources* 12(3), 4867-4880. DOI: 10.15376/biores.12.3.4867-4880

Sharma, A., Balda, S., Gupta, N., Capalash, N., and Sharma, P. (2020). "Enzyme cocktail: An opportunity for greener agro-pulp biobleaching in paper industry," *Journal of Cleaner Production* 271(1), article 122573. DOI: 10.1016/j.jclepro.2020.122573

Strunk, P., Oeman, T., Gorzsas, A., Hedenstroem, M., and Eliasson, B. (2011). "Characterization of dissolving pulp by multivariate data analysis of FT-IR and NMR spectra," *Nordic Pulp and Paper Research Journal* 26(4), 398-409. DOI: 10.3183/npprj-2011-26-04-p398-409

Sutradhar, S., Sarkar, M., Nayeem, J., Jahan, M. S., and Tian, C. (2018). "Potassium hydroxide pulping of four non-woods," *Bangladesh Journal of Scientific and Industrial Research* 53(1). DOI: 10.3329/bjsir.v53i1.35903

Yang, C., Niu, Y., Su, H., Wang, Z., Tao, F., Wang, X., Tang, H., Ma, C., and Xu, P. (2010). "A novel microbial habitat of alkaline black liquor with very high pollution load: Microbial diversity and the key members in application potentials," *Bioresource Technology* 101(6), 1737-1744. DOI: 10.1016/j.biortech.2009.09.092

Yu, O., and Kim, K. H. (2020). "Lignin to materials: A focused review on recent novel lignin applications," *Applied Sciences – Basel* 10(13), article 4626. DOI: 10.3390/app10134626

Yuan, H. Y., Wu, S. B., Yin, X. L., Huang, Y. Q., Liu, H. C., Wang, G. J., Zhan, H., and Wu, C. Z. (2018). "Silicon distribution in straw black liquor recovery process of pyrolysis and combustion," *CIESC Journal* 69(5), 2191-2198.

Article submitted: June 6, 2024; Peer review completed: June 30, 2024; Revised version received: July 12, 2024; Accepted: July 13, 2024; Published: July 19, 2024.
DOI: 10.15376/biores.19.3.6160-6177