Preliminary Study on Pulping of Rice Straw in Tris-(2-Hydroxyethyl) Ammonium Acetate Ionic Liquid under Microwave Irradiation

Xuemei Han,[a] Manman Tang,[a] and Yu Deng [a,b,*]

This study investigated the pulping process of cooking rice straw in tris-(2-hydroxyethyl) ammonium acetate ionic liquid under microwave irradiation. The optimal processing conditions were determined *via* othogonal experimentation based on analyses of the effects of the main factors, namely the mass ratio of ionic liquid to rice straw, cooking time, and microwave power, on the cooking of pulp. Those conditions are as follows: mass ratio of ionic liquid to rice straw 5:1, cooking time 30 min, and microwave power 350 W. When subsequent verification experiments were conducted under the conditions above, the pulp yield was as high as 47.28%, the ionic liquid was able to be recycled, and the recovery was as high as 96.9%. The physical properties of the paper confirmed that paper of satisfactory commercial quality could be produced using this technology.

Keywords: Ionic liquid; Microwave irradiation; Pulping; Rice straw

*Contact information: a: School of Materials Science and Chemical Engineering, Tianjin University of Science & Technology, Tianjin, P. R. China 300457; b: Tianjin Key Laboratory of Pulp & Paper, Tianjin, P. R. China 300457; *Corresponding author: dengyu@tust.edu.cn*

INTRODUCTION

Traditionally, the pulp and paper industry is a high-consumption, high-pollution industry that produces a pulping wastewater known as “black liquor.” This pollution load accounts for about 80% of the total wastewater produced from papermaking and has become the main source of the pollution associated with the papermaking industry, due to the presence of lignin, short chain cellulose, inorganic chemicals (spent pulping chemicals), and other organics (Huang and Ramaswamy 2011). Researchers are continuing to explore new pulping technologies, such as altering the cooking solvents and cooking methods, with the aim of reducing the emissions to zero.

Ionic liquids (ILs) are chemicals composed of an organic cation and an inorganic or organic anion with a melting temperature below 100 °C at atmospheric pressure. (Kubisa 2009). ILs have some advantageous properties, such as low toxicity, good dissolvability, excellent microwave absorbance, high ionic conductivity, good thermal stability, and recyclability. In 2002, Swatloski *et al*. reported that ILs could be used as non-derivatizating solvents for cellulose, mainly because anions are strong hydrogen bond acceptors. Since then, many studies on the dissolution of cellulose and other biopolymers in ILs have been reported, such as those regarding cellulose (Cuissinat *et al.*

2008; Du *et al.* 2011; Liu *et al.* 2012; Casasa *et al.* 2012), collagen (Meng *et al.* 2012), starch (Mateyawa *et al.* 2013), and glucose (Kim *et al.* 2012).

At present, microwave-assisted technology has been accepted as a rapid and convenient approach to many applications and has been widely used in pretreatment (Liu *et al*. 2010), organic synthesis (Ren *et al*. 2013), extraction (Fishman *et al*. 2006), and the paper industry (Palm and Zacchi 2003; Saha *et al*. 2011), due to its advantages of rapid heating rate, short reaction time, and high energy utilization. ILs interact very efficiently with microwave irradiation through the ionic conduction mechanism and can be quickly heated without any considerable pressure increase. Recently, Wang *et al*. (2013) studied the dissolution and delignification of wood in 1-ethyl-3-methylimidazolium acetate and found that microwave irradiation was an efficient method for breaking the strong hydrogen bonds that link cellulose, hemicelluloses, and lignin. Such treatment can facilitate the delignification of lignocellulosic biomass in ionic liquid and reduce the dissolution time significantly (Wang *et al*. 2013).

The pulping of rice straw in ionic liquid is a pulping technology that utilizes the unique solvent power of ionic liquids to retain cellulose and separate lignin. The pulping process of cooking rice straw in ionic liquid under microwave irradiation has the advantages of producing little pollutants, consuming minimal energy, and requiring only simple equipment. Furthermore, the solvent can be easily extracted and recycled after the pulping, which is of great significance due to the cost reduction this permits. This study investigated the optimum conditions for the pulping of rice straw in tris-(2-hydroxyethyl) ammonium acetate ionic liquid under microwave irradiation.

EXPERIMENTAL

Materials and Instruments

The rice straw materials were provided by Tianjin Key Laboratory of Pulp & Paper, China. The chemical composition of the rice straw was determined to be conducted according to the method described by Shi and He (2006). The results were as follows: 33.5% cellulose, 73.6% holocellulose, 20.2% pentosans, 0.91% acid-soluble lignin, 22.7% Klason lignin, 2.89% alcohol-benzene extractives, 16.3% ash, and 7.56% moisture. Tris-(2-hydroxyethyl) ammonium acetate ionic liquid was synthesized according to previously reported procedures (Yuan *et al*. 2007).

Methods

Pulping process

The pulping process used in this study is shown in Fig. 1.

Cooking rice straw for pulping

Before pulping, the rice straw was cut into small sections of 25 to 30 mm in accordance with *Analysis and Determination for Pulp and Paper* (Shi and He 2006) and dried. A total of 10 g of dry rice straw was put into a three-necked flask. The contents of three flasks, each containing a quantity of ionic liquid based on a given mass ratio of ionic liquid to rice straw, were mixed well. The pulping experiments were conducted at different microwave powers for different amounts of time. After cooking, the rice straw was poured into a 200-mesh filtration bag and repeatedly washed with distilled water in order to separate out the ionic liquid. The liquid solution was transferred into a beaker and kept static for some time to allow for precipitation, then centrifuged at 3000 rpm and filtered. Finally, the precipitated lignin was washed repeatedly with the appropriate amount of distilled water before being dried and weighed.

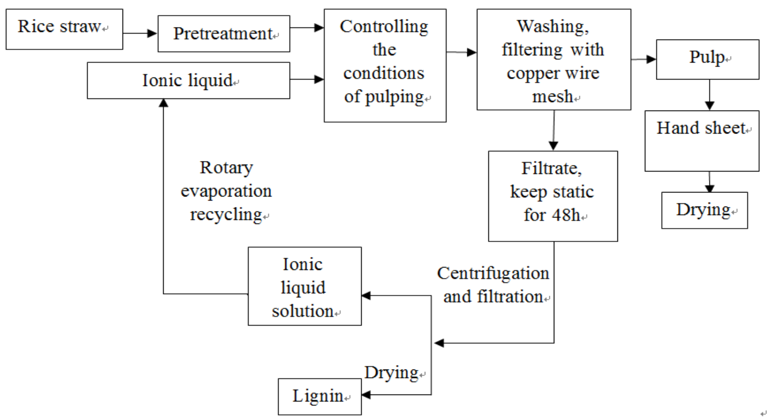

Fig. 1. Pulping process scheme

Screening, beating, and papermaking

The rice straw fiber, after being washed, was screened with a square pulp screen (slit width = 0.2 mm) and squeezed to dryness in a mesh bag until the pulp concentration was about 25%. After the moisture balance of the pulp had been reached, a PFI mill was used for beating until the pulp concentration was 10% and the beating degree was 45 °SR. Then, a standard disintegrator was applied for 15,000 revolutions. A standard sheet former (7407S type, Mavis Engineering Ltd., Britain) was used according to the TAPPI method, and the produced sheets were measured as 60 g/m^2. The produced sheets were dried in a drum dryer after being subjected to the front press for 5 min and to the back press for 3 min. Then the sheets were stored in an environment of constant temperature and humidity (23 ± 1 °C, 50 ± 2% RH) for 4 h. Then the physical properties of the produced sheets were tested.

Characterization

Scanning electron microscope (SEM) images were obtained using a JMS-6380LV emission scanning electron microscope. The pulp of the film was sputter-coated with gold and then observed and imaged.

X-ray diffraction (XRD) was performed on a TD-3500 X-ray diffractometer with Cu Kα radiation (2θ = 1.54178 Å). The 2θ range was from 10° to 80° in steps of 0.04°.

The tightness, tear index, burst index, and breaking length of the produced paper were tested according to the standards GB/T 451.2-1989, GB/T 455.1-1989, GB/T 454-1989, and GB/T 453-1989, respectively.

Recycling of ionic liquid

After filtration, the washing liquor and its filtrate were heated, which, by removing the moisture *via* rotary evaporation, allowed the ionic liquid to be recovered for further use. Then, the recovery of the ionic liquid was calculated. If the initial amount of ionic liquid was m_0 (g), and the quality of recycled ionic liquid was m (g), then the recovery of ionic liquid was calculated as follows:

$$w = \frac{m}{m_0} \times 100\% \tag{1}$$

RESULTS AND DISCUSSION

Unifactor Experiments

Effect of the mass ratio of ionic liquid to rice straw on the pulp yield and the delignification percentage

The effect of the mass ratio of ionic liquid to rice straw on the pulp yield and the percentage delignification was investigated by cooking various amounts of rice straw in ionic liquid under the microwave power of 300 W (about 100 °C) for 20 min. With the increase in the mass ratio of ionic liquid to rice straw, the pulp yield initially increased and then decreased, reaching the maximum when the mass ratio was 6:1 (Fig. 2). In the case of the lower mass ratios, the rice straw was not able to be pulped due to incomplete soaking, and part of the rice straw was carbonized. Meanwhile, the percentage delignification increased with increases in the mass ratio and reached its height when the mass ratio was 6:1, although there was no obvious change after 6:1. Thus, it was recommended that the selected mass ratio of ionic liquid to rice straw be 6:1.

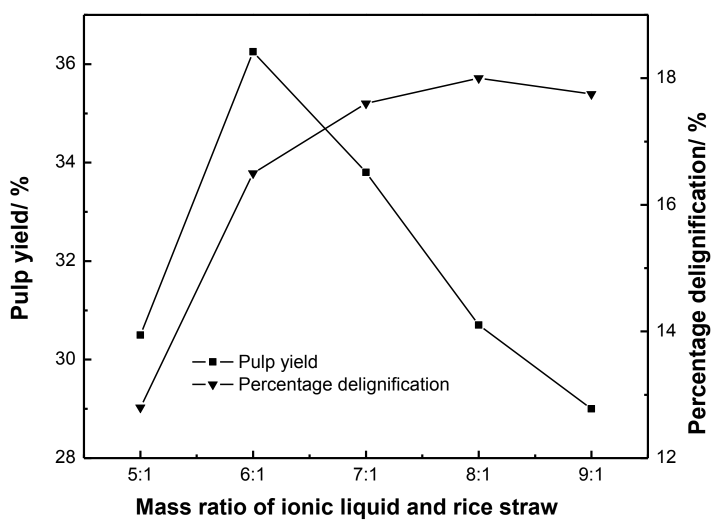

Fig. 2. Effect of mass ratio of ionic liquid to rice straw on the pulp yield and the delignification percentage

Effect of the cooking time on the pulp yield and the percentage delignification

The effect of the cooking time on the pulp yield and the percentage delignification was studied by cooking the rice straw in ionic liquid in a mass ratio of 6:1 under the microwave power of 300 W for various lengths of time. With the extension of the cooking time, the pulp yield and the percentage delignification initially increased and then decreased, the pulp yield reaching its maximum at 25 min of cooking time, while the percentage delignification reached its largest value when the cooking time was 30 min (Fig. 3). In the case of the shorter cooking times, the lignin was not able to be adequately dissolved, while part of the cellulose was dissolved and degraded with the extension of the time. Given the results for both pulp yield and percentage delignification, it was recommended that the cooking time selected be 25 min.

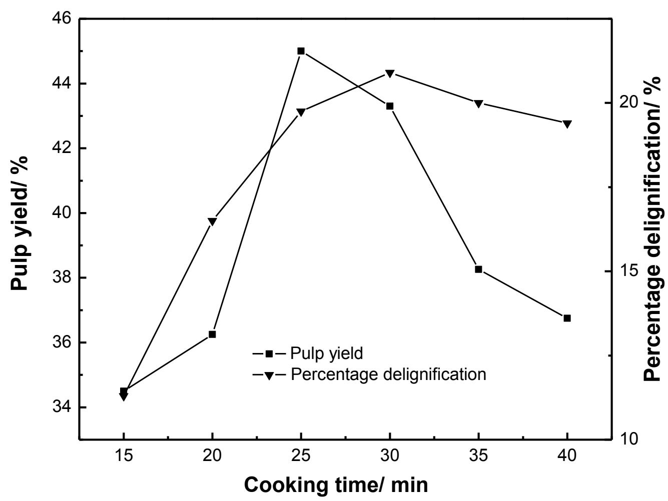

Fig. 3. Effect of cooking time on the pulp yield and the delignification percentage

Effect of the microwave power on the pulp yield and the percentage delignification

The effect of microwave power on the pulp yield and the percentage delignification was studied by cooking rice straw in ionic liquid in a mass ratio of 6:1 for 25 min under varying microwave powers. With the increase in microwave power, the pulp yield and the percentage delignification at first increased and then decreased. The pulp yield reached its maximum when microwave power was 300 W, and the percentage delignification reached its largest value at the same microwave power (Fig. 4). At the lower microwave powers, the rice straw was not able to be boiled completely, while higher microwave powers resulted in serious degradation and carbonization of the carbohydrate (Huang *et al*. 2008). Therefore, taking into account both pulp yield and the percentage delignification, the suitable microwave power was established to be 300 W.

Orthogonal Experimentation

To obtain the optimal pulping conditions, orthogonal experiments were carried out, as reported in Table 1.

According to the range R analysis, the primary and secondary sequences of factors influencing pulp yield were determined to be as follows: mass ratio of ionic liquid to rice straw > microwave power > cooking time. It was deemed intuitively plausible that the maximum pulp yield was 45.5% in experiment No. 3 and that the most effective set of processing conditions was $A_1B_3C_3$: mass ratio of ionic liquid to rice straw 5:1, cooking time 30 min, and microwave power 350 W.

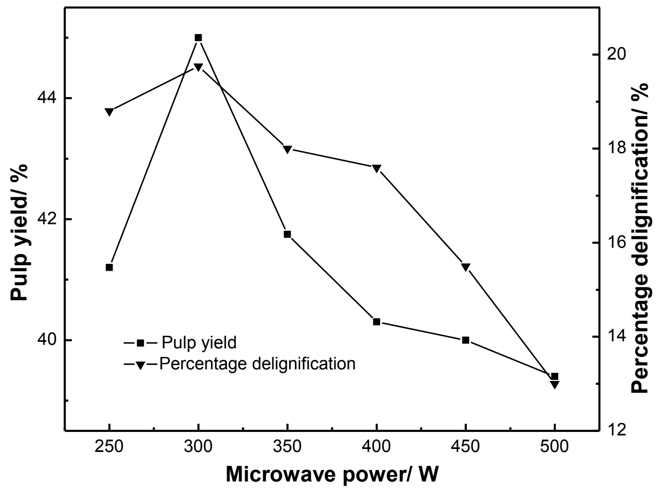

Fig. 4. Effect of microwave power on the pulp yield and the delignification percentage

Table 1. The Orthogonal Experiments

No.	A Mass ratio of ionic liquid to rice straw (g/g)	B Cooking time (min)	C Microwave power (W)	Pulp yield (%)
1	5:1	20	250	33.0
2	5:1	25	300	39.0
3	5:1	30	350	45.5
4	6:1	20	300	25.0
5	6:1	25	350	29.5
6	6:1	30	250	25.0
7	7:1	20	350	35.5
8	7:1	25	250	31.6
9	7:1	30	300	33.2
K_{I}	117.5	93.5	89.6	
K_{II}	79.5	100.1	97.2	
K_{III}	100.3	103.7	110.5	
R	38	10.2	20.9	

Verification Experiments under the Optimal Processing Conditions

Verification experiments were conducted under the optimal processing conditions in recycled ionic liquid. The resulting pulp yield and ionic liquid recovery values are shown in Table 2. As seen in Table 2, the ionic liquid recovery was as high as 96.9%, while the pulp yield was as high as 47.28%, indicating that the pulp yield did not change when recycled ionic liquid was used.

Table 2. Verification Experiments

No.	1	2	3
Pulp yield (%)	46.64	47.98	47.23
Ionic liquid recovery (%)	97.1	96.4	97.2

Fiber Property Analysis

As shown in Fig. 5, most of the fibers were very short. The proportion of fibers having length under 1 mm was approximately 85%.

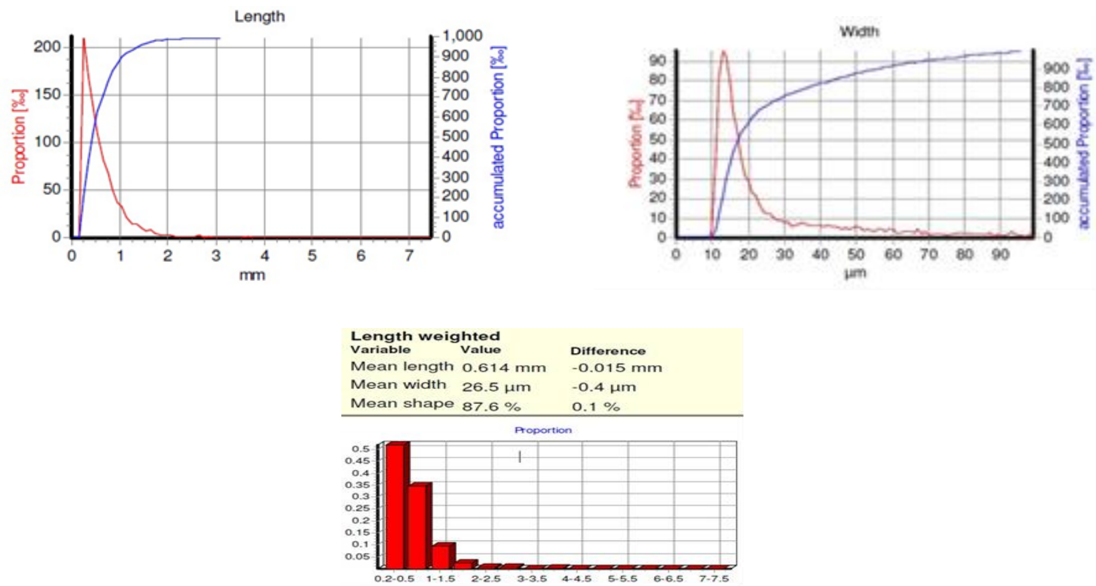

Fig. 5. Property analysis of pulp fibers

SEM Analysis

As shown in Fig. 6, fibrillation occurred in the pulp fibers. The cell walls of the fibers were broken, and more micro fibers were exposed. Such phenomena as kinks, curls, and depressions appeared amongst the fibers.

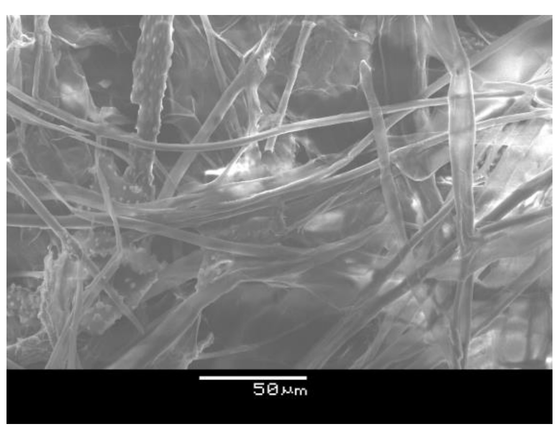

Fig. 6. SEM image of pulp fibers

XRD Analysis

XRD analysis was conducted on the pulp fibers cooked in ionic liquid under microwave irradiation, and the results are shown in Fig. 7. The characteristic diffraction peaks (2θ = 15.554°, 2θ = 21.842°) matched well with the standard pattern associated with type I cellulose, which indicated that there was no obvious change in the crystal structure of the rice straw cellulose after pulping in tris-(2-hydroxyethyl) ammonium acetate ionic liquid.

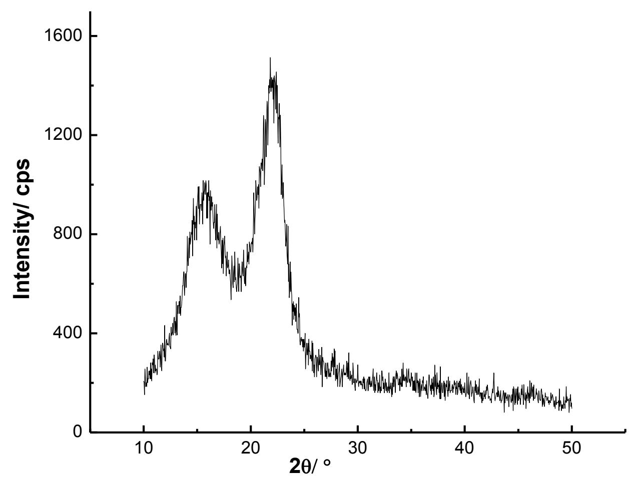

Fig. 7. XRD analysis of the pulp fibers

Tests of Physical Properties of Paper

The results from the physical properties test of the paper were as follows: apparent density 0.434.3$\times 10^5$ g/m^3, tear index 1.72 mN·m^2/g, burst index 1.31 kPa·m^2/g, and breaking length 2.98 km.

CONCLUSIONS

1. A new rice straw pulping process, which utilizes tris-(2-hydroxyethyl) ammonium acetate ionic liquid under microwave irradiation and which does not produce black liquor, was studied. Paper was successfully produced using this process.

2. The optimal processing conditions were obtained by way of unifactor and orthogonal experiments. Under the optimal conditions, the pulp yield was 47.28%, indicating that the pulp can be classified as general chemical pulp.

3. The ionic liquid was successfully reused, with a recovery of around 96.9%, which could significantly mitigate the high cost.

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