Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(8):260-263

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Microwave pulping process for rice straw in basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$

Wei Song[1], Yu Deng*[2], Ying Xu[3] and Mingxian Cui[4]

[1]*Tianjin Key Laboratory for Control Theory & Applications in Complicated Systems, Tianjin University of Technology, Tianjin, China*
[2]*School of Materials Science and Chemical Engineering, Tianjin University of Science &Technology, Tianjin, China*
[3]*Tianjin Key Laboratory of Pulp & Paper, Tianjin University of Science &Technology, Tianjin, China*
[4]*Tianjin Key Laboratory for Control Theory & Applications in Complicated Systems, Tianjin University of Technology, Tianjin, China*

ABSTRACT

This paper makes study of microwave pulping process for rice straw in basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$. Ionic liquid is synthesized and the experiments are carried out on pulping process. The pulp yields are close to 40%. It belongs to the high yield chemical pulp. The average recovery rate of ionic liquid is 94%, which makes pulping process no pollution, that is, no black liquor. Test results show that the paper properties satisfy the general requirements of paper. XRD result indicates that rice straw cellulose crystal type is no obvious change after ionic liquid microwave cooking pulping. The damage degree of rice straw fiber is small. SEM analysis shows that the basic ionic liquid has a strong penetration under the supplementary role of microwave radiation. There is no significant difference for pulp fiber morphology by microscope observation after cooking pulping as well as and fiber length&width detection. These results show that the microwave pulping process for rice straw in basic ionic liquid is in line with the grasses pulping characteristics.

Key words: microwave, ionic liquid; rice straw; pulping process; lignin

---

INTRODUCTION

Traditional pulping technology is not only a waste of drug resources, large energy consumption, high cost, serious pollution, and the reaction time is long, the pulp yield is low [1-3]. So it makes the pulp and paper industry development hindered seriously. For traditional organic solvent pulping process, it generally uses the flammable solvents with low boiling point as cooking agent. In the pulping process, low boiling point solvent needs generally a higher pressure [4-8]. Ionic liquid is a new type of green solvents, which has strong dissolving ability, low vapor pressure and other superior performances. Ionic liquids are used as pulping cooking agent for pulping and papermaking process, it will eliminate black liquid from the source of pollution, and make straw pulp green pulping process [9-11]. This paper researches the microwave pulping process for rice straw in basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$, tests the physical properties of paper sheet, and analysizes the change of cellulose crystal type and fiber morphology in pulping process. Results show that the microwave pulping process for rice straw in basic ionic liquid is in line with the grasses pulping characteristics. The grasses solvent pulping with ionic liquids to replace the traditional organic solvent will become a new research direction to improve the pulping process.

EXPERIMENTAL SECTION

2.1 Materials

Triethanolamine, chemically grade, from Tianjin chemical reagent wholesale company; ice acetic acid and absolute ethyl alcohol, analysis of pure, from Tianjin Fuchen Chemical Reagent Factory; rice straw, from pulping and papermaking laboratory of Tianjin University of Science and Technology.

2.2. Synthesis ionic liquid

Put solvent absolute ethyl alcohol into 250ml three-mouth flask, which contains a stirrer, thermometer and condenser. Then add triethanolamine and ice acetic acid (molar ratio1:1.1) which are preheated at 25℃. The adding sequence is that adds triethanolamine firstly, then opens stirrer, and drops of ice acetic acid slowly. After ice acetic acid being dropped completely, the reactants keep reacting 20h under room temperature. After ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$ is synthesized, it will be diluted to 70% (mass fraction), and put in brown reagent bottle. This is the cooking liquor.

2.3 Microwave cooking experiments [12,13]

Put a clean rice straw and ionic liquid in a reactor inside microwave oven. After cooking, put the rice straw pulp into 200 mesh filter bag, rinse repeatedly it with distilled water and squeeze out cooking liquor in the end. Transfer liquid phase to a beaker, remain still for a period of time. Lignin is separated out again by centrifugal separation after a large amount of precipitate being separated out. It is rinsed repeatedly with distilled water, dried and weighed. Ionic liquid is recycled by filtering, washing, distillation, drying, weighing after cooking pulping.

2.4 Fiber-pulp-treatment

Rice straw fiber being washed is screened using square pulp screen (the seam width of 0.2 mm), and dehydrated to the pulp concentration of about 25% in the cloth bag. After moisture of pulp stock gets equilibrium, beating pulp using a Beater(ZQS2-23, machinery factory of Northwest Institute of Light Industry, China) until beating pulp concentration 10%, beating pulp degree of 45°SR, then defibering it 15000-turn with standard deflaker.

2.5 Paper physical properties test

Using standard paper sheet forming device (7407S, Mavis Engineering Ltd, UK), the ration of papermaking is 60 g/m^2 page sheet according to TAPPI method. Formed paper sheet is dried on a drum dryer after going through 5 min front and 3 min back surfaces press. Handsheet is placed in the environment of constant temperature and humidity （23±1℃；50±2%RH）4 hours, then tested physical performances [14,15]. According to the national standard GB/T 2679.5-1995/1989, paper physical properties are tested by Swedish L&W company determinators of bursting strength, tearing strength and breaking length.

2.6 SEM scanning and XRD diffraction analysis

XRD (TD-3500, Dandong Tongda Technology Co., LTD, China) surveys cellulose crystal type changes after cooking pulping. The fiber structure and morphology characteristics of rice straw can be observed by SEM (EM-30, Beijing Kusaimu Scientific Instruments Marketing Center, China) scanning as well as a Universal Research Microscope after ionic liquid cooking pulping.

RESULTS AND DISCUSSION

3.1 Microwave cooking experiments and Paper performance test

Put 30g (1.5cm) rice straw and ionic liquid$[NH\text{-}(C_2H_4OH)_3]+$ into the reactor according to solid-liquid ratio of 1:5. Microwave power is 350W, cooking time is 30min. Cooking experiments are repeated three times at atmospheric pressure and reflux conditions. The pulp yields are close to 40%. The average recovery rate of ionic liquid is 94% by three parallel experiments. The results are shown in Table 1.

Table 1 Cooking experiment results of pulping process

Experiment	1	2	3	Average
pulp yield (%)	38	39	41	39.3
Recovery rate of ionic liquid (%)	93	95	96	94.5

The pulp yield of rice straw cooking pulping in ionic liquid is higher than conventional chemical pulping due to the unique properties of ionic liquid dissolving lignin. Cooking agent ionic liquids can be recycled, which overcome its disadvantage of the expensive and make pulping process no pollution, that is, no black liquor. These prove that this method can not only greatly shorten the cooking time, improve the efficiency of cooking, and speeding up the chemical reaction and dissolution of lignin. This will provide a new development space for the pulp paper industry.

Paper sheet of experiment preparation is shown in Figure 1. Results of paper physical properties test are displayed in Table 2. Test results show that paper properties satisfy the general requirements of paper.

Table 2 Paper physical properties test

test item	results	test item	results
tearing index	1.72mN·m^2/g	lignin content	18%
brust index	0.81kpa·m^2/g a	tightness	0.43 g/m^2*um
breaking length	1.8km	polymerization degree	781

Figure1 Paper picture of experiment preparation

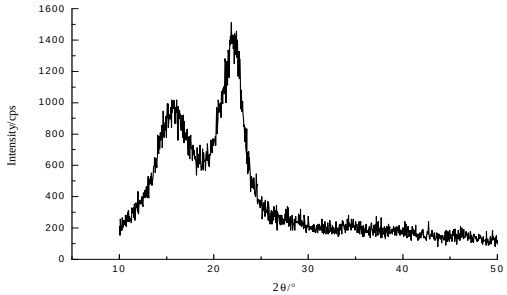


Figure 2 XRD diffraction pattern of pulp fibers

3. 2 XRD diffraction analysis

The rice straw pulp fibers are analyzed by XRD after microwave cooking, as shown in Figure 2. These characteristic diffraction peaks (2 θ =15.554 °, 2 θ =21.842 °) corresponded to standard spectrum diagram of □type natural cellulose. It illustrates that rice straw cellulose crystal type is no obvious change after ionic liquid microwave cooking pulping. The damage degree of rice straw fiber is small.

3.3 SEM scanning pulp fiber

The paper sheet fibers are scanned by SEM after microwave cooking, which is shown in Figure 3.

We can see that crosslinking degree of paper fibers is better and fiber shape is more complete. Most of fibers are relatively stiff, part of them appear different degree of curl and kink. This could be due to basic ionic liquid [NH-(C2H4OH)3]+ has a strong penetration under the supplementary role of microwave radiation. That makes part of the cell wall peel and fibers come up the devillicate phenomenon. As fiber cell wall thinning and stiffness decrease, some fibers are no longer a tubular, but a strip shape, therefore they are easy to curl and kink.

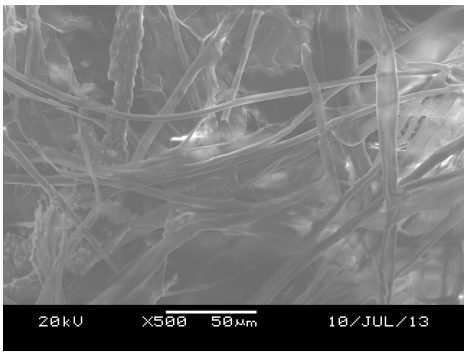


Figure 3 SEM scanning pattern of paper fiber

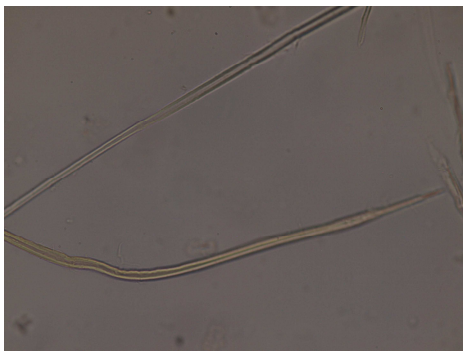


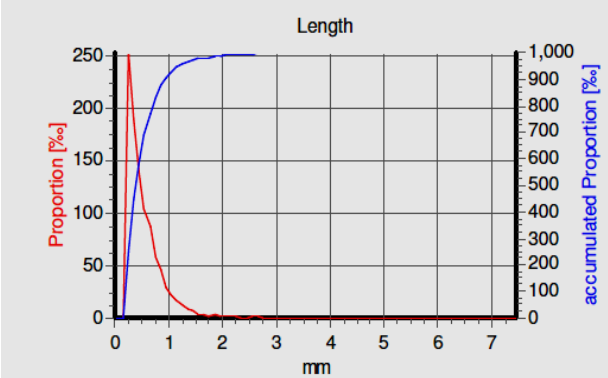
Figure 4 Fiber morphology of paper pulp

3.4 Analysis fiber morphology of paper pulp

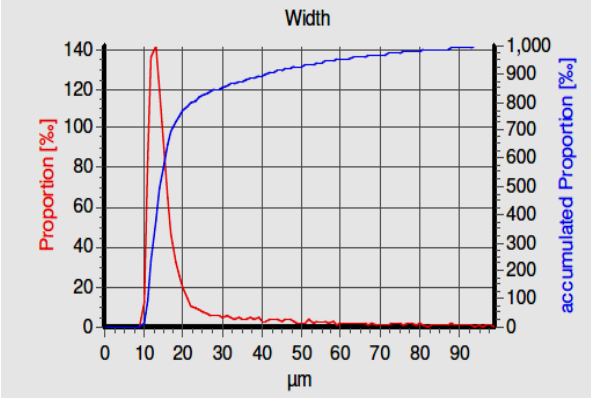
The fiber morphology of paper pulp is observed under a Universal Research Microscop after microwave cooking rice straw in basic ionic liquid, as shown in Figure 4. It is seen from Figure 4 that there is no significant difference for pulp fiber morphology, and fibers are small and soft, which are in line with straw pulp characteristics.

3.5 Length-width distribution of fibers

The pulp fibers are dispersed by beating pulp after microwave cooking. The fiber length of the pulp is detected 0.552mm, fiber width 21.3μm. Length-width distribution of fibers is shown in Figure 5,6. The figures show that the pulp fibers are mainly fine ones after basic ionic liquid microwave cooking rice straw pulping.



Fiber 5 Distribution proportion of fiber length



Fiber 6 Distribution proportion of fiber width

CONCLUSION

1. The pulp yields are close to 40% in microwave pulping process for rice straw in basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$ when microwave power 350W, cooking time 30 min. It belongs to the high yield chemical pulp. The average recovery rate of ionic liquid is 94%, which makes pulping process no pollution, that is, no black liquor. These prove that this method can not only greatly shorten the cooking time, improve the efficiency of cooking, and speeding up the chemical reaction and dissolution of lignin. The paper properties satisfy the general requirements of paper.

2. XRD indicates that cellulose crystal type is still possessed the configuration of Ⅰ type cellulose after microwave cooking rice straw in basic ionic liquid, as the same as natural rice straw cellulose crystal type. SEM pattern shows that basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$ has a strong penetration under the supplementary role of microwave radiation. That makes part of the cell wall peel and thin. As fibers come up the devillicate phenomenon and stiffness decrease, some fibers is no longer a tubular, but a strip shape.

3. There is no significant difference for pulp fiber morphology by a Universal Research Microscop observation after basic ionic liquid microwave cooking rice straw, and fibers are small and soft, which are in line with straw pulp characteristics. The pulp fibers are dispersed by beating pulp after microwave cooking. The fiber length of the pulp is detected 0.552mm, fiber width 21.3μm. The pulp fibers are mainly fine ones.

Acknowledgment
The authors would like to thank the National Natural Science Foundation of China for providing financial support for this project (21176195).

REFERENCES

[1] SJ Zhang; XQ Yao; et al. *SCIENCE IN CHINA PRESS, B: CHEMIST*RY, **2009**, 39(10), 1134-1144.
[2] Y Zheng; XP Xuan; AR Xu, *Progress in Chemistry*, **2009**, 21(9), 1807-1812.
[3] CF Liu; WY Li; RC Sun; J Ye, *Paper Science & Technology*, **2007**, 26(6), 37-40.
[4] B Li; F Ilari; DS Argyropoulos, *Industrial & Engineering Chemistry Research*, **2010**, 49(7), 3126-3136.
[5] D A Fort; R C Remsing; R P Swatloski, *Green Chem*, **2007**, 9(1), 63-69.
[6] C Li, *World Pulp and Paper*, **2005**, 28(1), 14-17.
[7] YH Tian; DC Li; DL Gong, *Hubei Agricultural Sciences*, **2012**, 51(6), 1228-1231.
[8] HR Gong, *Paper Chemicals*, **2007**, 19(6), 26-28.
[9] KC Nakamata, *JAPAN TAPPI JOURNAL*, **2013**, 67(12), 1367-1371.
[10] YJ Xu; J Wang, *China Pulp & Paper*, **2011**, 30(06), 46-48.
[11] H B Xie; A King; I Kilpelainen; et al. *Biomacromolecules*, **2007**, 8(12), 3740-3748.
[12] YH Liu, Y Deng, *Transactions of the Chinese Society of Agricultural Engineering (CSAE)*, **2009**, 25(9), 259-263.
[13] HL Gan; HP Shang; Y Deng, *China Pulp & Paper Industry*, **2009**, 30(16), 48-50.
[14] M Makiv; P Aksela, WO, 017001[P].**2005**.
[15] SL Shi; FW He. Analysis and Detection of Pulping and Paper, 1st Edition, China Light Industry Press, Beijing, **2003**, 50-78.