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Research Article

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

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ABSTRACT

This paper makes study of pulping process for rice straw in basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$. The pulp yields increases with extended time, which the concentration of residual lignin in rice straw pulp gradually declines. The results indicate that the temperature 100 ℃ and time 60min are suitable for cooking pulping. Separated lignin is scanned by IR and fiber analysis. Triethanolamine ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$ can well dissolve lignin which contains large number of hydroxyl groups. The lignin with lilacs and guaiac structures has the better dissolving performance at 100 ℃. It is known that fiber length is 0.758mm, width 22.8μm by detecting its size. The pulp fibers are mainly fine ones, which are in line with straw pulp characteristics.

Key words: Ionic liquid; Lignin; Rice; Pulping; Fiber

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]. It makes the pulp and paper industry development hindered seriously. In recent years, ionic liquids as a new type of environmentally friendly solvents, more and more get the attention of people [5, 6]. Ionic liquid pulping process not only can improve the selectivity of cooking reagent, make it easier for lignin dissolution, shorten the cooking time, reduce the consumption of chemicals, also cuts down the pollution load of black liquor [7-10]. This research includes the synthesis of ionic liquids, cooking experiments of different reaction temperature, reaction time, and extracted rough lignin is scanned by infrared and fiber analysis under different reaction conditions.

EXPERIMENTAL SECTION

2.1 Materials

Triethanolamine, analytical grade, Tianjin North Tianyi Chemical Reagent Factory; glacial acetic acid , analytical grade, from Tianjin Fuchen Chemical Reagent Factory; anhydrous ethanol, analytically pure, Tianjin shibei fine chemicals development co., LTD; rice straw, from pulping and papermaking laboratory of Tianjin University of Science and Technology.

2.2. Synthesis ionic liquid

Put solvent anhydrous ethanol into 250ml three-mouth flask, which contains a stirrer, thermometer and condenser. Then add triethanolamine and ice acetic acid according to the ratio of 1:1.1 after preheating at 25℃. After adding triethanolamin, turn on the stirrer, dropping ice acetic acid slowly till completely finished [11, 12]. It takes 20 h to react at room temperature, the reaction equation is as follows:

$N(CH_2\text{-}CH_2\text{-}OH)_3+CH_3COOH \rightarrow [NH\text{-}(CH_2\text{-}CH_2\text{-}OH)_3]^+ + [CH_3COO]^-$

2.3 Rice straw cooking pulping

Cut rice straw to 1.5cm pieces before cooking. Every time take 20g oven dry straw. Then add them and ionic liquid into digester according to the solid-liquid ratio of 1:5, and mix evenly. Cooking experiments are carried out in different temperature & cooking time at atmospheric pressure [13].

2.4 Lignin separation

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. Make centrifugal separation after a large amount of precipitate being separated out. The filtrate pH is adjusted neutral after the precipitate separated out undergoing alkali soluble and acid soluble. Lignin is separated out again in neutral solution. It is rinsed repeatedly with distilled water, dried and weighed [14].

2.5 Infrared analysis

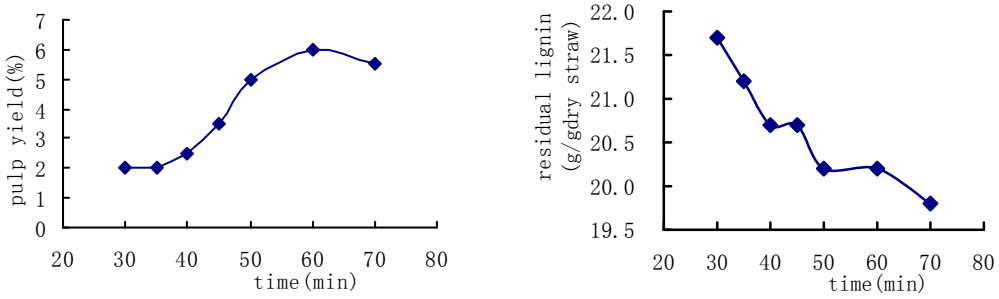
Infrared spectrum are carried out using KBr pellets and recorded on WQF-510 FTIR spectrophotometer, the instrument resolution of $4cm^{-1}$, the scanning number is 16, the scanning range is $500 \sim 4200cm^{-1}$.

RESULTS AND DISCUSSION

3.1 Effects of cooking time on pulping process

3.1.1 Effects of cooking time on pulp yield and residual lignin of rice straw pulp

Effects of different cooking time on pulp yield and residual lignin of rice straw pulp are shown in figure 1 under the conditions: 20g oven dry straw, liquid-solid ratio 5:1, temperature 100℃.



(a) **(b)**

Figure 1 Effects of time on pulp yield and residual lignin

It can be seen from figure 1 (a) that the pulp yields show a trend of rising with extended time. It increases slowly in the early time and then rapid growth because a lot of fiber is dispersed to the cooking liquor after a period of time. Prolonging the cooking time makes the reaction more fully. In the late of the chemical reaction, the dispersed cellulose occur decomposition because of reaching the cooking limit under the experimental conditions. Figure 1 (b) shows that the longer the cooking time, the smaller the concentration of residual lignin in rice straw pulp. Comprehensive consideration pulp yields and the amount of residual lignin, appropriate cooking time is 60min.

3.1.2 Effects of cooking time on the infrared structure of the lignin

The infrared spectra of lignin are shown on Figure 2 (these curves are the spectra of 30, 40, 50 and 60min respectively from top to bottom). Figure 2 shows that (1) at 3397 (1/cm), stretching vibration relative strength of hydroxyl (OH^-) is largest. It can be speculated that that the lignin of high hydroxyl content is dissolved and separated out in a large amount and retain the activity of the functional groups. The relative intensity appears the tendency of decrease as the extended cooking time. It may be due to the ionic liquid damage the structure of the hydroxyl during the reaction process. Seeing 1226 (1/cm) phenol hydroxyl relative strength, the changing rules are roughly the same. (2) At 1700 (1/cm), the relative absorption strength of carbonyl (C = O mainly ester bond carbonyl) changes unobvious, only there is a decrease at the 60 min. Here is connected the lignin hydroxyl structure to other structural unit in the form of ester bond. This connection structure vibration is stronger for a long time. It shows that long time is in favor of the lignin dissolving out. (3) At 1328 (1/cm) of lignin phenol ether bond (Ar - O), the change of relative strength of absorption peak is not obvious. It can be concluded that there are lilacs lignin dissolved out with the extension of time, and it has a tendency to increase, but the amount of increase is not big. From 1029 (1/cm), we can see the relative strength also decrease gradually with time. It may make fatty ether bond of side chain fracture in a certain degree during the cooking process. (4) At 1421 (1/cm) of C-H on the lignin $-OCH_3$, it can be seen that stretching vibration changes unobvious in a short time till 60 min. This indicates that it can

increase methoxyl content of black liquor only cooking a long time. (5) At 835 (1/cm), it can be seen that special C-H vibration of aromatic ring associated with guaiacol lignin is obviously on the 2, 6 place outside plane. But this vibration appears a trend of decrease with time, and the minimum intensity is at 60 min. It explains that guaiacol lignin can be dissolved easily for a long time cooking.

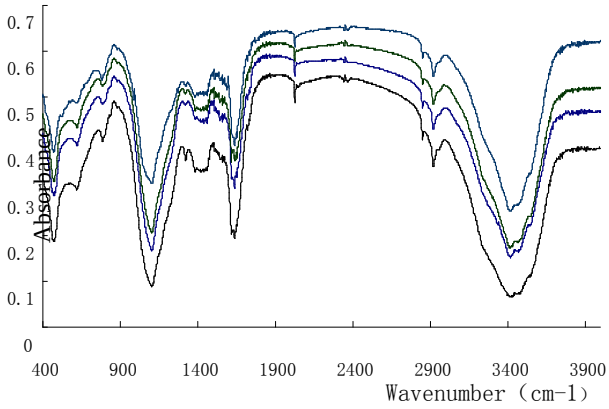
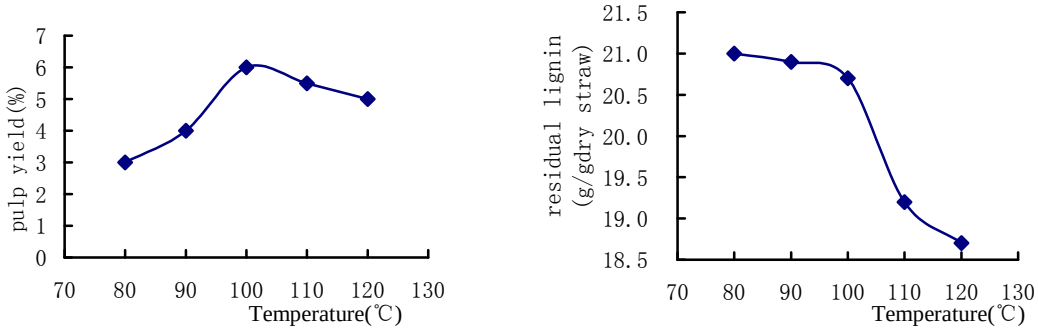


Figure 2 The IR spectrogram of lignin under different time

3.2 Effects of cooking temperature on pulping process

3.2.1 Effects of cooking temperature on pulp yield and residual lignin of rice straw pulp Effects of different cooking temperature on pulp yield and residual lignin of rice straw pulp are shown in figure 3 under the conditions: 20g oven dry straw, liquid-solid ratio 5:1, time 60min. It can be seen from figure 3 (a) that the pulp yields increases with temperature rise gradually, then gradually decreases before 100℃. The reason is that the rice straw does not come to boiling at the low temperature. Only high temperature can make structure of straw fiber damaged and cellulose more easily dispersed. In the late of the chemical reaction, cellulose may decompose in the process of cooking, and even dissolve. Figure 3 (b) shows that residual lignin content reduces gradually with temperature rise, but reduce speed obviously different. Straw does not come to boiling at low temperature, so less lignin dissolved. But the dissolution rate decreases when temperature is too high. As the result 100℃ is suitable for lignin dissolution



(a) **(b)**

Figure 3 Effects of temperature on pulp yield and residual lignin

3.2.2 Effects of cooking temperature on the infrared structure of the lignin

Figure 4 shows the infrared spectra of lignin at 80℃, 100℃, 110℃ and 120℃ respectively (from top to bottom).The lignin functional strength is not the same when the temperature is different. (1) At 3397 (1/cm), stretching vibration relative strength of hydroxyl (OH-) decreases along with the cooking temperature, but it's slightly higher at 120℃. It indicates that lignin which contains more hydroxyl is dissolved and separated out in a large amount and retains the activity of its functional groups. The changing rules of relative strength are roughly decreases gradually at 1226 (1/cm) phenol hydroxyl. (2) At 1700 (1/cm), the relative strength of carbonyl (C=O mainly ester bond carbonyl) changes unobvious. Here is connected the lignin hydroxyl structure to other structural unit in the form of ester bond. (3) At 1328 (1/cm), the change of stretching vibration of lignin phenol ether bond (Ar-O) is not obvious. The relative intensity is smaller at 100℃. It can be concluded that the lignin dissolubility is the largest, and the lilacs lignin can be determined. From 1029 (1/cm), we can see the relative strength of absorption is minimum at 100℃ and it appears increase at high temperature. That means higher temperature cooking may make fatty ether bond of side chain fracture in a certain degree. (4) At 1421 (1/cm) of C-H in methoxyl group, it can be seen that stretching vibration change unobvious and is smaller at 100. It shows that this temperature is much better

for methoxyl group dissolving out. (5) At 835 (1/cm), it can be seen that special C-H vibration of aromatic ring associated with guaiacol lignin is obviously on the 2, 6 place outside plane. Relative absorption intensity is also small at 100℃. It explains that this temperature is more appropriate and can determine dissolved out lignin contains more guaiac lignin

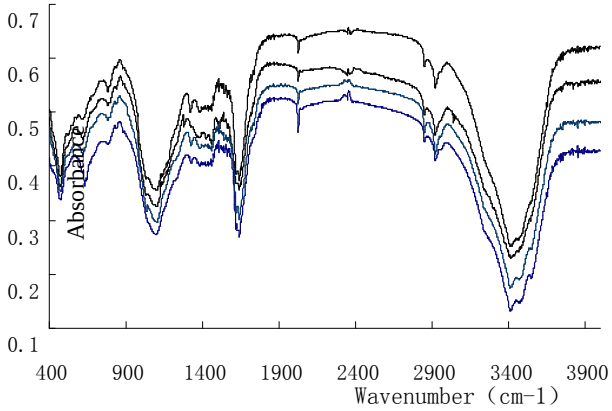


Figure 4 The IR spectrogram of lignin under different temperature

Through the IR analysis of the relative strength of absorption peak, we understand that triethanolamine ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$can well dissolve lignin which contains large number of hydroxyl groups. The lignin with Lilacs and guaiac structures has the better dissolving performance at 100℃.

3.3 length & width of the pulp fiber

After cooking under the conditions of liquid- solid ratio 5:1 of ionic liquid to rice, cooking temperature 100℃, cooking time for 60min, the treatments of beating pulp and dispersing are carried out. We detecte the size of the pulp fibers and get its length is 0.614mm, fiber width 26.5μm. The results show that the pulp fibers are mainly fine ones after cooking pulping, which is in line with straw pulp characteristics.

CONCLUSION

(1) Considering the effects of cooking temperature and time on pulping process of basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$ cooking rice straw based on the pulp yield and residual lignin in rice straw pulp, we can conclude that the cooking temperature 100℃ and cooking time 60min are suitable for cooking pulping. The pulp yields increases with extended time, which the concentration of residual lignin in rice straw pulp gradually declines.

(2) Through the IR analysis, we understand that triethanolamine ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$can well dissolve lignin which contains a large number of hydroxyl groups. The lignin with lilacs and guaiac structures has the better dissolving performance at 100℃.

(3) The pulp fibers are dispersed by beating pulp after basic ionic liquid $[NH\text{-}(C_2H_4OH)_3]^+$cooking rice straw pulping. It is known that fiber length is 0.758mm, width 22.8μm by detecting its size. The pulp fibers are mainly fine ones, which are in line with straw pulp characteristics.

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