Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(5):831-835

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Ionic liquid cooking wheat straw pulping and delignification reaction kinetics

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ABSTRACT

In this paper, the pulping process of wheat straw in the acidic ionic liquid N - methyl imidazole hydrosulfate is analyzed. The pulp yields can be stabilized at about 50% under the optimum process conditions by 3 times repetitive verification experiments. The boiling solvent ionic liquid can be recycled repeatedly, and its average recovery is 89.2%. Effects of cooking temperature and time on delignification and the lignin structure change are discussed by the infrared examines during the pulping process. XRD diffraction analysis of cooked wheat straw pulp fibers indicates that the cooking process is mild without causing damage to the cellulose. Delignification reaction kinetics of the ionic liquid N - methyl imidazole hydrosulfate cooking wheat straw pulping has been carried on preliminary discussion.

Key words: ionic liquids, process conditions, infrared examines, cooking, kinetics

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INTRODUCTION

Traditional pulping technology is the general method which is applicable to non wood fiber pulping process [1-3]. This method 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. So it makes the pulp and paper industry development seriously hindered [4-9]. The grasses solvent pulping with ionic liquids to replace the traditional organic solvent will become a new research direction to improve the pulping process [10-12]. Researches have shown that the ionic liquids have a stable performance, no pollution, easy to recycle, and can increase reaction rate, reveal good catalytic performance in the homogeneous reaction medium experiments [13-15]. This paper studies the pulping process of wheat straw in acidic ionic liquid N- methyl imidazole hydrosulfate. Effects of cooking temperature and time on delignification and the lignin structure change are discussed by the infrared examines during the pulping process. The delignification process is discussed under the different cooking temperature and time variables.

EXPERIMENTAL SECTION

2.1 Materials

N- methyl imidazole, chemical grade, Tianjin chemical reagent wholesale company; concentrated sulfuric acid, chemical grade, Tianjin North Tianyi Chemical Reagent Factory; sodium hydroxide, analysis of pure, from Tianjin Fuchen Chemical Reagent Factory; wheat straw, from pulping and papermaking laboratory of Tianjin University of Science and Technology.

2.2. Synthesis ionic liquid

Add a certain amount of N - methyl imidazole in three-mouth flask, and drip equimolar concentrated sulfuric acid under the condition of ice water bath. Stir and react for 24 h at 10 ℃. Then wash it repeated with a small amount of ethyl acetate. The pale yellow transparent sticky ionic liquid is obtained after rotary evaporation and vacuum drying

at 80℃.

2.3 Wheat straw cooking pulping

Cut wheat straw to 2-3 cm pieces and put it into digester. Add N - methyl imidazole hydrosulfate liquid according to a certain ratio of liquid-solid. Analyze the effects of different cooking temperature and time variables on wheat straw pulping [16].

2.4 Separating lignin and recycling ionic liquid

After cooking, put the wheat straw pulp into 200 mesh filter bag, and make ionic liquid separated. Then rinse repeatedly wheat straw pulp with distilled water. Transfer liquid phase to a beaker, let it still for a period of time. Make centrifugal separation after the precipitate being separated out. The filtrate pH is adjusted neutral after the precipitate separated out undergoing alkali-soluble, separation, acid-soluble. Lignin is separated out again in neutral solution. It is rinsed repeatedly with distilled water, dried and weighed. Ionic liquid is recycled by filtering, washing, distillation, drying, weighing after cooking pulping.

2.5 Infrared and XRD diffraction analysis

Infrared spectrum are carried out using KBr pellets and recorded on WQF-510 FTIR spectrophotometer, the instrument resolution of 4 cm - 1, the scanning number is 16, the scanning range is 500 ~ 4200 cm - 1. XRD (TD-3500, Dandong Tongda Technology Co., LTD, China) surveys cellulose crystal type changes after cooking pulping.

RESULTS AND DISCUSSION

3.1 Ionic liquid N - methyl imidazole hydrosulfate cooking wheat straw pulping

Effects of cooking variable on pulping process have been researched by single factor and orthogonal experiments. Based on calculating pulp yield and analysis of range R, we obtained that the influence degree of various factors on pulp yield was cooking temperature > liquid-solid ratio > cooking time. Verification experiments repeated 3 times under the condition of temperature 130℃, liquid-solid ratio 8:1, time 30min, and the average pulp yield is 50%. The average recovery rate of ionic liquids is 89.2% by three parallel experiments.

3.2. Infrared spectroscopic analysis

3.2.1 The influence of cooking temperature on the lignin structure

The infrared spectra of lignin are shown on Figure 1 after cooking time 30 min, when liquid-solid ratio is 8:1，wheat straw cooking temperature 110℃, 130℃ and 140℃ respectively. Figure 1 shows that (1) at 3400 (cm^{-1}), stretching vibration relative strength of hydroxyl (OH^-) reflects that the dissolubility of lignin appears the tendency of increase gradually as cooking temperature. It can be found that higher temperature is advantageous to the lignin removal; (2) at 1600 (cm^{-1}), the relative absorption strength of carbonyl (C = O mainly ester bond carbonyl) has a little change with temperature; (3) at 1421 (cm^{-1}), methoxy C-H vibration increases gradually with temperature rise. It shows that higher temperature is advantageous to the removal of methoxyl group; (4) at 1262 and 835 (cm^{-1}), it can be seen that vibration relative strength of guaiacol type lignin decreases with temperature rise, and the strength of vibration at low temperature is bigger. It explains that guaiac lignin is easy to dissolve out as the main composition of lignin, and decompose gradually with the increase of temperature. That causes its strength will be reduced.

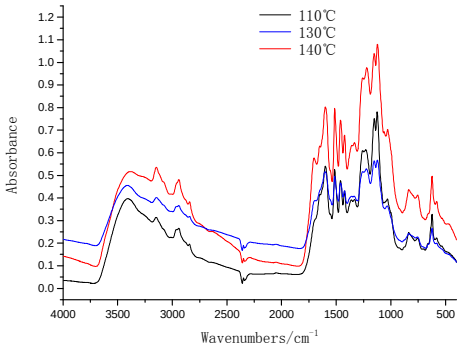

Figure 1 Lignin IR spectra under different temperature

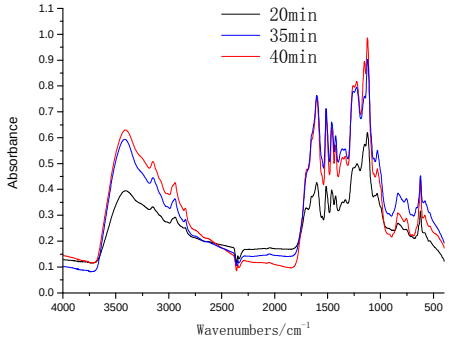

Figure 2 Lignin IR spectra under different time

3.2.2 The influence of cooking time on the lignin structure

The infrared spectra of lignin are shown on Figure 2 when liquid-solid ratio is 8:1， cooking temperature 130℃, cooking time 20min, 35min, 40min respectively. Figure 2 shows that (1) at 3400 (cm^{-1}), stretching vibration

relative strength of hydroxyl (OH^-) reflects that the relative intensity appears the tendency of decrease as the extension of cooking time. It can be found that the lignin is decomposed and hydroxy damaged as the extension of cooking time; (2) at 1600 (cm^{-1}), the relative absorption strength of carbonyl (C = O mainly ester bond carbonyl) reflects that quantity of hydroxyl lignin separation gradually increases with the extension of cooking time and its content is nearly constant after 35 min; (3) at wave numbers of 1330 and 1120-1124 (cm^{-1}), relative vibration strength of lilacs type lignin can reflect that the relative strength of lilac aldehyde decreases gradually. It explains that a large number of lilacs type lignin has been dissolved into the cooking liquor at the beginning of the reaction. The lilacs type lignin dissolved out comes up to decompose at a certain extent as the extension of cooking time; (4) at 1262 (cm^{-1}) and 835 (cm^{-1}), it can be seen that the vibration relative strength of guaiacol type lignin has a little change with the extension of time.

3.3 XRD diffraction analysis

Pulp fibers are carried on XRD diffraction scanning after cooking. Effects of ionic liquid N- methyl imidazole hydrosulfate on cellulose crystal type are inspected in cooking wheat straw process. The results are shown in figure 3. The characteristic diffraction peak (2 θ =22.499 °) corresponds to standard diffraction pattern of natural cellulose[17]. It indicates that the ionic liquid has certain effect to dissolve cellulose. The pulping process is mild without causing damage to the cellulose.

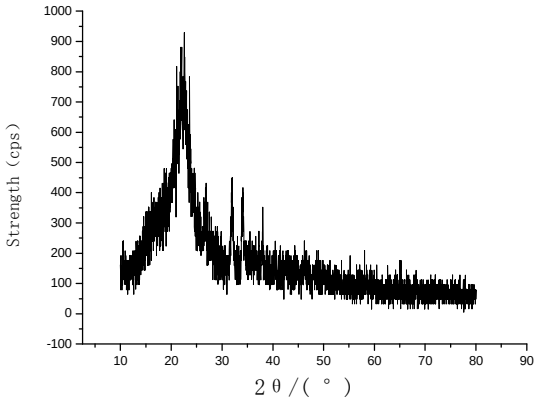

Figure 3 XRD analysis of pulp fibers

3.4 Delignification reaction kinetics

The condition of removal lignin with ionic liquid is mild, only under the normal pressure. Ionic liquid can dissolve lignin of wheat straw, and react with dissolved lignin as the reaction reagent at the same time, which cause lignin decomposition. Kinetics experiments are carried on respectively in 80℃, 90℃, 100℃, 110℃, 12 ℃, 130℃ for ionic liquid N - methyl imidazole hydrosulfate cooking wheat straw pulping. The percentage changes of lignin quality relative to dry raw material over time are measured before and after wheat straw cooking. The results are shown in table 1.

Table 1 The lignin concentration in pulp

L	80℃	90℃	100℃	110℃	120℃
0min	0.318	0.318	0.318	0.318	0.318
10min	0.288	0.268	0.258	0.218	0.198
15min	0.279	0.258	0.251	0.178	0.158
20min	0.268	0.248	0.248	0.173	0.148
25min	0.258	0.241	0.208	0.158	0.138
30min	0.228	0.198	0.138	0.153	0.078

The linear fitting equations between -dL/dt and lignin content L at different temperatures are obtained by differential processing of the data in Table 1. Results are shown in table 2. These fitting coefficients are very close to 1. This proves again that the reaction is first order. When cooking temperature rises, the lignin removal rate constants increase. That is to say high temperature is more conducive to delignification.

Table 2 Regression equations of lignin removal rate and kinetics

T/℃	relation	R^2
80	-dL/dt =0.0306L-0.0333	0.9563
90	-dL/dt =0.033L-0.3414	0.9732
100	-dL/dt =0.0417L-0.401	0.9735
110	-dL/dt =0.039L-0.2373	0.9918
120	-dL/dt =0.0435L-0.1399	0.9798
130	-dL/dt =0.0478L+0.0367	0.9856

Relationship between the reaction rate constant k and reaction temperature is consistent with Arrhenius[18] formula, namely $\ln k = \ln k_0 - \frac{E_a}{RT}$ where k—reaction rate constant, min^{-1}; k_0—frequency factor, min^{-1}; Ea—reaction activation energy, kJ/mol; T—reaction temperature, K; R—universal gas constant, 8.314J/(mol · K).

Make removal rate constant k linear fitting about 1/T in order to calculate activation energy. Equation lnk=0.1269-1280.1/T is obtained after linear regression, its fitting coefficient R^2 is 0.9972. The activation energy *Ea* is calculated to be 10.645 $kJ \cdot mol^{-1}$ by substitution the gas constant into this equation.

CONCLUSION

（1）pulping experiments give that the pulp yields can be stabilized at about 50% under the optimum process conditions (temperature 130℃, liquid-solid ratio 8:1, time 30min), which belong to high yield chemical pulp. The boiling solvent ionic liquid can be recycled repeatedly, and its average recovery is 89.2%.

（2）It can be found that the guaiac lignin is the main ingredients of wheat straw lignin by the infrared examines lignin structure change in the process of cooking, and easy to be removed in pulp cooking. XRD diffraction analysis indicates that the ionic liquid N- methyl imidazole hydrosulfate has certain effect to dissolve cellulose, and the pulping process is mild without causing damage to the cellulose.

（3）Ionic liquid can dissolve lignin of wheat straw, and react with dissolved lignin as the reaction reagent at the same time, which cause lignin decomposition. The kinetics experiments present that delignification reaction kinetics of acidic ionic liquid N- methyl imidazole hydrosulfate cooking wheat straw pulping is first order, thereinto fitting coefficient R^2 is 0.9972, and its reaction activation energy is 10.645 kJ·mol-1.

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

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