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Delignification reaction kinetics for wheat straw in neutral ionic liquid 1-methyl-3-ethyl bromide imidazole

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ABSTRACT

In this paper, neutral ionic liquid 1 - methyl - 3 - ethyl bromide imidazole [Emim]Br is synthesized. The effects of cooking temperature and time on pulping process are analyzed based on the pulp yield. It can be concluded that the cooking temperature 90-130℃ and cooking time 60 min are suitable for research of delignification reaction kinetics. The pulp yields steady at about 40%, which belongs to high yield chemical pulp. The physical properties of papersheet, which is prepared by ionic liquid cooking wheat pulping, satisfy the general requirements of paper. Kinetics experiments are carried out under the temperature 90℃, 100℃, 110℃, 120℃, 130℃ respectively. The results gives that delignification reaction kinetics of ionic liquid pulping process belongs to first order, its reaction activation energy is 57.938kJ·mol-1.

Key words: delignification; kinetics; ionic liquids; cooking; wheat straw; pulping

INTRODUCTION

Traditional pulping technology is the general method which is applicable to non wood fiber pulping process [1-4]. For 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 generally needs a higher pressure, which the corresponding temperature arrives at 180-220℃. This method is not only 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 [5-7]. Ionic liquid is a new type of green solvents, which has been found in recent years. It has strong dissolving ability, low vapor pressure and other superior performances [8-10]. The grasses solvent pulping with ionic liquids to replace the traditional organic solvent will become a new research direction to improve the pulping process [11-13]. It can not only greatly shorten the cooking time, improve the efficiency of cooking, speeding up the chemical reaction and dissolution of lignin, greatly improve production efficiency, reduce the cost, and expect to achieve the maximize use of plant fiber resources value in the field of pulp and paper [14-17]. This paper studies delignification process during pulping process for wheat straw in neutral ionic liquid 1 - methyl - 3 - ethyl bromide imidazole [Emim]Br. Results show that the pulping process is in line with the grasses pulping characteristics. This study will provide new ideas and method for innovation and development of papermaking technology.

EXPERIMENTAL SECTION

2.1 Materials

N- methyl imidazole, chemically grade, Tianjin chemical reagent wholesale company; ethyl bromide, 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 N- methyl imidazole and ethyl bromide (molar ratio1:1.3) into a four-necked round bottom flask. Heating and reflux in the water bath, simultaneously mechanical stirring. When temperature was slowly raised to 60℃., heating was stopped. The solution gradually became turbidity from colorless, then to light yellow transparent liquid, and viscosity increased gradually. After a certain reaction time, the excess ethyl bromide was distilled off with a rotary evaporator, to give a pale yellow or colorless transparent liquid. Let it stand for a period of time, the white or pale yellow crystals was precipitated, i.e. ionic liquid [Emim]Br.

2.3 Wheat straw cooking pulping

Wheat straw was cut to 2-3 cm pieces and put into digester. Ionic liquid was added according to a certain ratio of liquid-solid. Analyses of the effects of cooking variables on pulping process under atmospheric pressure were made [18].

2.4 Fiber-pulp-treatment

Wheat 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 performance test

Using standard paper sheet forming device (7407S, Mavis Engineering Ltd, UK), the ration of papermaking is 34.4 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. According to the national standard GB/T 2679.5-1995/1989, paper physical properties are tested by Swedish L&W company determinators. The limiting viscosity number of the pulp is determined by test of copper ethylenediamine viscosity method

RESULTS AND DISCUSSION

3.1 Effects of cooking variables on pulping process for wheat straw in Ionic liquid

1. Effects of cooking temperature on pulping process

Effect of different cooking temperature on pulp yield was shown in figure 2 under the conditions of liquid-solid ratio 10:1 and time 60 min. The pulp yield increased with temperature rise gradually, while it began decreased over 140℃. Referred to related literatures to know that the straw lignin contains a large number of phenolic hydroxyl and carboxyl groups, and more p-hydroxyphenyl units connects with other lignin structure unit in the form of ester bond. Under mild conditions, the ester bond in lignin could be completely broken, and a-ether bond also fractured partly. That made the straw lignin fragmented and easily dissolved [19,20]. Therefore, selected cooking temperature should be able to remain sufficient delignification rate in pulping process, that was, to reduce the damage rate of cellulose.

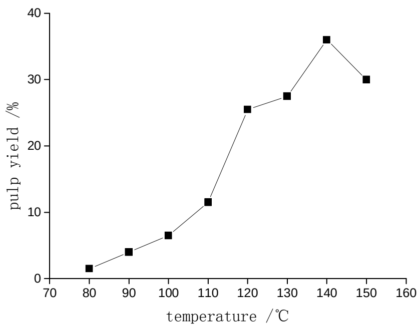

Figure 1 Effects of different cooking temperature

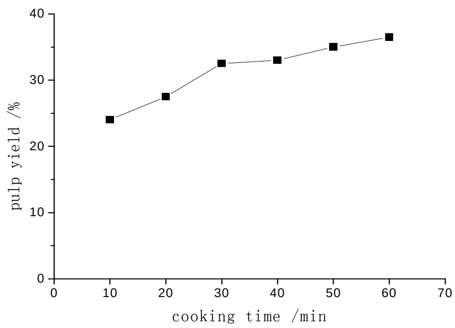

Figure 2 Effects of different cooking time

2. Effects of cooking time on pulping process

Effect of different cooking time on pulp yield was shown in figure 3 under the conditions of liquid-solid ratio 10:1 and temperature 120℃.. The pulp yield increased firstly with extension of cooking time, then leveled off. Wheat straw cooking reaction belonged to fast dissolving stage during 10-30 min and a lot of lignin dissolved out at this stage. This trend generally leveled off after 30 min. Technically speaking, the longer the cooking time is, the more completely cooking reaction, the more deeply degree of delignification. But in the late cooking, that was, after most of lignin had been removed out, cellulose macromolecules were completely exposed in ionic liquid. These caused cellulose degraded easily, productivity reduced and energy consumption increased.

3.2 Paper physical properties test

Paper physical properties test included pulp defibering, beating (45°SR) and handsheet. Paper sheet of experiment preparation is shown in figure 3. Its physical properties were determined (see table 1). Test data indicated that physical properties of the paper meet the requirements of general paper for wheat straw cooking pulping process in ionic liquid.

Figure 3 Paper picture of validation experiment

Table 1 Paper properties test

test item	results	test item	results
tightness	0.547 $g.cm^{-3}$	tearing strength	1.43mN·m^2/g
breaking length	1.61km	bursting strength	0.59 kP_a·m^2/g
Pulp polymerization degree（DP）	724.9		

3.3 Delignification reaction kinetics

The condition of removal lignin with ionic liquid is mild. 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. The conditions of kinetics experiments are determined to liquid-solid ratio of 10:1, cooking time for 60 min, cooking temperature 90-130℃ based on above experiments.

1. Determination of reaction order

Kinetics experiments are carried out respectively at 90℃, 100℃, 110℃, 120℃ and 130℃ for ionic liquid [Emim]Br cooking wheat straw pulping. The percentage changes of lignin quality relatively to dry raw material over time are shown in table 2.

Table 2 Lignin content of cooking process (relatively dry raw material)

L/ g/g	90℃	100℃	110℃	120℃	130℃
0min	15.9	15.9	15.9	15.9	15.9
10min	15.14	14.63	13.83	13.13	12.59
20min	14.39	13.46	12.04	10.84	9.976
30min	13.71	12.39	10.47	8.953	7.902
40min	13.04	11.4	9.114	7.394	6.259
50min	12.4	10.49	7.931	6.105	4.958
60min	11.8	9.65	6.901	5.042	3.927

Powell method is used to determine the reaction order. According to the theory of reaction kinetics, the kinetics equation of chemical reaction can be expressed as:

$$-\frac{dL}{dt} = kL^n$$

n$\neq 1$, $$\frac{1}{n-1}\left(\frac{L^{1-n}}{L_0^{\ 1\text{-}n}} - 1\right) = kL_0^{n-1}t$$

n=1, $$\ln\frac{L}{L_0} = -kt \qquad (1)$$

where, L—residual lignin content g/g (to dry raw material); t—cooking time, min; k—reaction rate constant; n—reaction order; L_0—lignin content in the raw material g/g (to dry raw material)

define: $$\alpha = \frac{L}{L_0}$$

$$\tau = kL_0^{n-1}t \qquad (2)$$

therefore: $$\alpha^{1-n} - 1 = (n-1)\tau$$

For different reaction orders n, α are calculated corresponding to different τ. α—τ curves are drawn, namely Powell curve as shown in figure 4.

Taking logarithm to equation (2), we have: $$\lg\tau = \lg k + (n-1)\lg L_0 + \lg t \qquad (3)$$

k, n, L_0 are fixed value for a specific chemical reaction, and only time t is variable. Therefore, to determine a reaction order, just need to measure α and τ under different time. Drawing α—τ curves and making this curve lateral movement a distance. Let the experimental curve overlap Powell curves in the same reaction order, and decide reaction order directly according to Powell curves.

Table 3 The value of α&τ of cooking process

t/min	90℃		100℃		110℃		120℃		130℃	
	τ	α	τ	α	τ	α	τ	α	τ	α
10	0.05	0.952	0.083	0.92	0.139	0.87	0.191	0.826	0.233	0.792
20	0.099	0.905	0.166	0.847	0.278	0.757	0.383	0.682	0.466	0.627
30	0.149	0.862	0.25	0.78	0.417	0.659	0.574	0.563	0.699	0.497
40	0.199	0.82	0.332	0.717	0.557	0.573	0.766	0.465	0.932	0.394
50	0.249	0.78	0.416	0.66	0.696	0.499	0.957	0.384	1.165	0.312
60	0.298	0.742	0.499	0.61	0.835	0.434	1.149	0.317	1.398	0.247

Lignin content L and reaction time t, which have been measured in pulping process of wheat straw, are substituted into the above formula (1) and (3). Values of α and τ can be obtained during the process of cooking (see table 3). After these data are made a drawing, this drawing is translated to figure 4 (see figure 5). It is found from figure 5 that the curve from experimental data points is identical perfectly with the Powell curve when n = 1. That explains that this reaction is first order.

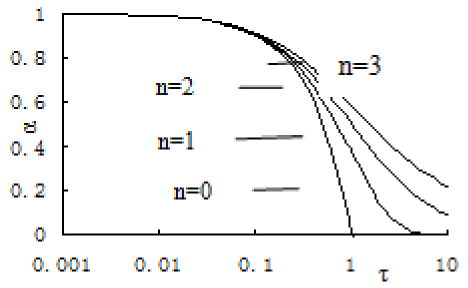

Figure 4 Powell curves

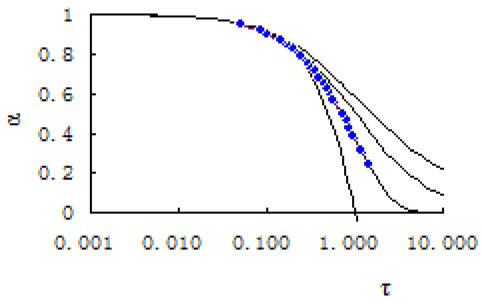

Figure 5 Powell curves of delignification

2. The determination of the reaction rate constant and activation energy
The relationship between dL/dt and t are shown in table 4. The linear fitting equations between -dL/dt and lignin content L at different temperatures are obtained by differential processing data in table 5. The 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 4 The relationship between dL/dt and t during cooking process

t/min	90℃		100℃		110℃		120℃		130℃	
	L	-dL/dt	L	-dL/dt	L	-dL/dt	L	-dL/dt	L	-dL/dt
0	15.90	0.077	15.9	0.127	15.9	0.207	15.9	0.277	15.9	0.331
10	15.13	0.075	14.63	0.122	13.83	0.193	13.12	0.253	12.59	0.296
20	14.40	0.072	13.46	0.112	12.04	0.168	10.84	0.209	9.976	0.235
30	13.70	0.068	12.39	0.103	10.47	0.146	8.953	0.172	7.902	0.186
40	13.03	0.068	11.40	0.095	9.114	0.127	7.393	0.142	6.259	0.147
50	12.40	0.062	10.49	0.087	7.930	0.111	6.105	0.118	4.958	0.117
60	11.80	0.060	9.653	0.084	6.900	0.103	5.042	0.106	3.927	0.103

Table 5 Regression equations of delignification Reaction Kinetics

T/℃	Regression equations	R^2
90	-dL/dt =0.004L+0.0104	0.9636
100	-dL/dt =0.007L+0.0113	0.9912
110	-dL/dt =0.0123L+0.0167	0.9896
120	-dL/dt =0.0168L+0.0208	0.98755
130	-dL/dt =0.203L+0.0236	0.9854

Relationship between the reaction rate constant k and reaction temperature is consistent with Arrhenius[21] 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 rate constant lnk linear fitting about 1/T in order to calculate activation energy (see figure 6). Equation lnk=13.698-6967•1/T is obtained after linear regression, its fitting coefficient R^2 is 0.9892. The activation energy *Ea* is calculated to be 57.938kJ·mol^{-1} by substitution the gas constant into this equation.

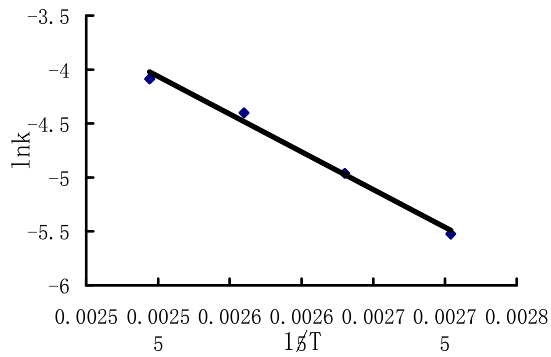

Figure 6 Relationship of lignin removal rate constant and temperature

CONCLUSION

(1) Considering the effects of cooking temperature and time on pulping process of ionic liquid [Emim]Br cooking wheat straw based on the pulp yield, we can conclude that the cooking temperature 90-130℃ and cooking time 60 min are suitable for research of delignification reaction kinetics. These pulp yields steady at about 40%, belong to high yield chemical pulp. The paper properties satisfy the general requirements of paper for ionic liquid cooking wheat straw pulping.

(2) 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 ionic liquid [Emim]Br cooking wheat straw pulping is first order, thereinto fitting coefficient R^2 is 0.9892, and its reaction activation energy is 57.938kJ·mol-1.

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