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CLEAN PRODUCTION OF CORN STOVER PULP USING KOH+NH_4OH SOLUTION AND ITS KINETICS DURING DELIGNIFICATION

Pulping of corn stover using KOH and NH_4OH was investigated. The combined alkaline system could effectively remove lignin during pulping. There are three stages of lignin removal during delignification. Approximately 90% of lignin could be removed after the temperature reached 150 °C for over 30 min. The p-hydroxyl phenol groups in lignin could be completely removed during the delignification reaction. The tendency of the increase of the crystalline degree of cellulose is observed with increase of reaction temperature. The kinetics of delignification are found to be first-order with respect to the remained lignin and 0.4 order with respect to the remaining hydroxide concentration. The activation energy of delignification is 23 kJ/mol. The solution obtained from precipitation of lignin is rich in nitrogen, phosphorous, potassium elements and organic matters. Various techniques including FT-IR, GPC, DSC, were applied to characterize the acid precipitated lignin. The result shows that the lignin with the polydispersity of 1.4 still maintains the p-coumaryl, coniferyl, and sinapyl units in its matrix.

Keywords: KOH+NH_4OH, corn stover, pulping, kinetics, lignin.

Corn is the third widely planted crop in China. The corresponding by-product corn stover is produced in large quantity annually [1]. One of the most widely adopted approaches for utilization of corn stover in China is to produce livestock feed [2]. With growing demand of paper pulp in developing countries such as China, production of paper using corn stover as a resource is regarded as one of the most profitable approaches for high-value conversion of such agricultural residues due to the shortage of wood derived resources in China [3]. The major technical hurdle of non-wood pulping is the pollution of the black liquor because of its poor performance of alkaline recovery.

The development of new pulping systems for solving straw based pulping has attracted a lot of attention recently [4,5]. Among them, pulping with KOH together with ammonia is regarded as one of the most cost-effective and promising approaches for integrated utilization of the produced black liquor [6]. Many kinds of feedstock such as wheat straw, rice straw, bagasse, etc., have been tested as the feedstock for pulping using such combined alkaline KOH + + NH_4OH systems [5-8]. However, using corn stover as feedstock together with this combined alkaline (KOH + NH_4OH) system, to the best of our knowledge, has rarely been published before. In addition, those results for combined alkaline-KOH + NH_4OH systems for non-wood biomass pulping are mainly based upon the employment of commercial KOH from chemical plants. The rather high price of KOH together with the long distance transportation makes this pulping process much less competitive and causes more CO_2 emission than the general process of using NaOH as the delignification reagent. Based upon our novel Acid/Base coupled production process [9], we have successfully produced K_2CO_3 and KOH with industrial grades on kilograms basis by the bench scale facility [10]. Our process, which is based on the recycling of boron salts and conversion of KCl together with the steam to the alkaline (K_2CO_3) and acid (HCl), is completely different from the current Chlor-alkali

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process. It is believed that this process is extremely suitable for the on-site utilization of biomass [11].

In the present paper, pulping of corn stover using our self-made KOH, the kinetics of delignification at different temperatures under the optimized condition, the characterization of corn stover reacted at different temperatures, the produced black liquor, acid precipitated lignin were closely investigated.

EXPERIMENTAL

Materials

The KOH used in this paper is made by causticizing reaction, with purity reaching industrial grade (92 wt.%, with impurity of boron oxide <2%, Ca< 1%, Cl<3%, Na<3%). The concentration of ammonia solution is 26 wt.%. The corn stover was harvested from the Hebei province in northern China and was cut into pieces approximately 5 cm in length. The normalized major composition percentages of the corn stover are shown in Table 1. The results show a general grass type precursor with relatively smaller lignin content and larger amount of ash and protein contents. This result indicates that the obtained corn stover could be used as raw material for paper making.

Table 1. Main compositions of corn stover

Component	Composition, wt.%
Cellulose	43.7
Hemicellulose	23.7
Lignin	12.5
Ash	5.0
Protein	11.2
Wax	3.8

Pulping experimental conditions

The experiment was conducted in a 1 L automatic mechanical stirring titanium autoclave system. Various experiments were conducted for exploring the effects upon pulp yield and delignification degree. The optimized conditions were obtained and are summarized as following: 50 g of dry corn stover was mixed with 5 g of KOH together with 45 g ammonia (26 wt.%) solution and diluted into 400 ml deionized water, then the slurry was put into the autoclave with mechanical stirring. The slurry was heated up from room temperature to 150 °C followed by further 30 min duration at this temperature.

After cooking, the black liquor was separated from the pulp by filtration and the pulp was washed thoroughly with water. The pulp was analyzed for delignification amount, pulp yield, pulp tear and tensile indices while the black liquor was analyzed for pH, COD, and lignin content. The contents of cellulose and hemicellulose were analyzed by the standard Van Soest method. The lignin content in biomass was analyzed by the Klason method. The Kappa value of the paper pulp, tensile and tear index, were measured according to standard method and the detailed experimental procedures can be found in the literature [3].

Chemical oxygen demand (COD) - Mn procedure: 1) 100 ml of sample in a 300 ml refluxing flask; 2) very slowly add 10 ml of H_2SO_4:water (1:2); 3) add 1 g Ag_2SO_4 (less than 1 g is possible) and mix well to dissolve, after 5 min the solution will become milky colored; 4) add 10 ml of $KMnO_4$ with accurate concentration of 0.025 N and mix; 5) attach flask to condenser and turn on cooling water system, boiling for 30 min; 6) disconnect reflux condenser, add 10 ml sodium oxalate $Na_2C_2O_4$ with concentration of 0.025 N; 7) titrate with solution of 0.025 M $KMnO_4$ from a burette, with a magnetic bar. During the titration, the temperature of solution was kept at around 60-80 °C.

Each experiment was performed in three replicates. There are 2-3% experimental uncertainties within all the experimental conditions.

Characterization of the raw material, paper pulp and lignin

FT-IR Analysis. A Spectrum GX (Perkin-Elmer USA 2003) infrared spectrometer was used for the study of the surface functional groups. Disc was prepared by mixing the 0.5 mg sample with 200 mg of KBr (Merck, for spectroscopy) in an agate mortar and then pressing the result mixture at 2 MPa for 1 min. The samples were scanned in the spectra range of 4000-370 cm^{-1}.

X-Ray diffraction (XRD) analysis. XRD Patterns were obtained with a Philips X'pert diffractometer using CuKα radiation at a wavelength of λ = 1.5406 Å, the thin powder sample was placed onto an oriented monocrystalline quartz plate and scanned from 10 to 90°.

Gel permeation chromatography (GPC) analysis. GPC analysis is conducted at the PE-Series 900 (Perkin-Elmer). The HR1, HR2 and HR3 styragel columns, RID 200 (refractive index detector) with flow rate of 1 ml/min and polystyrene as internal reference were adopted.

The elements Ca, B, K and Na were determined when 0.5 g prepared KOH was melted with ultra high purity nitric acid and then diluted to the fixed volume. ICP-OES (OPTIMA 5300DV Perkin-Elmer USA) was used for elements analysis.

TG/DSC Analysis. The differential scanning calorimetry was conducted on a TGA-50 (Shimadzu Japan) with a flow rate of 20 ml/min.

RESULTS AND DISCUSSION

Changes of lignin concentration in corn stover and solid yield during reaction

Lignin removal from corn stover during the delignification process is showed in Figure 1a. The main delignification process could be broadly divided into three stages. The first stage was a bulk delignification stage from the start to 100 °C, during which nearly 65% lignin from the corn stover was removed. Unlike wood delignification [12], the grass type material-corn stover, which possesses relatively larger percentage of HGS grass lignin, which mainly contains *p*-coumaryl, coniferyl, and sinapyl units in lignin matrix, makes it relatively easy for the alkaline (KOH and NH_4OH) to penetrate into the corn stover tissue matrix. The pH value dropped from 13.6 to 12.5 and effective alkaline dropped from 1.8 to 1.26 (mol/l), which is shown in Figure 1b, indicating the remaining of the un-reacted KOH in liquor at the end of the bulk delignification stage. The second delignification stage was a supplementary step starting from 100 to 150 °C (plus maintaining for 30 min). During this stage, approximately 15-19% of lignin was removed. The corn stover began to turn into pulp and the degree of delignification could reach over 85%. At the end of this stage, the pH further dropped to 11.6 suggesting some $[OH]^{-1}$ from KOH still exiting in solution. The last stage is the remaining phase until the end of reaction. Although the delignification degree could reach above 90%, the dramatic decrease of pulp yield occurred because of hydrolysis and decomposition of carbohydrates, which is due to the removal of lignin. Based on pH and effective alkaline value (1.03 mol/l), we could conclude that the active KOH is completely consumed at this stage and this agrees well with our result of the effect of amount of KOH added upon lignin removal and pulp yield.

Characterization of the paper pulp during reaction

The FT-IR spectroscopy of the corn stover solid at different temperatures is shown in Figure 2. The spectra of corn stover present the bands at 1630, 1140 and 835 cm^{-1}, which is the characteristic of the HGS grass lignin. With increase of reaction time, the intensity of those bands begins to decrease indicating the lignin removal during delignification. When the corn stover was treated at 150 °C for 30 min (sample 3), the spectra at 835 cm^{-1} disappeared, indicating that the *p*-hydroxyl phenol groups in solid were completely removed after reaction. The band of out plane vibration of glucose hexo-ring at 1400 and 900 cm^{-1} changes with the increase of temperature indicating that the structure of cellulose was also affected during reaction. The spectra of solid at different temperature presents the band at 1050 and 890 cm^{-1}, which represents the characteristic band of C-H bending vibration within plane of pentose. With increase of reaction temperature, intensity of those bands becomes decreased and band at 890 cm^{-1} in sample 3 even disappeared, indicating the effective removal of hemicellulose composite during the reaction. This result agrees with the characterization of black liquor that certain amount of pentose related debris exists in the black liquor, which contributes to the COD_{Mn} in black liquor.

The crystalline degree of the cellulose could be crystallographically characterized by means of X-ray diffraction, which is shown in Figure 3. The following equation could be adopted for calculation of the crystalline degree:

$$C = 100\frac{I_c}{I_c + I_a} \quad (1)$$

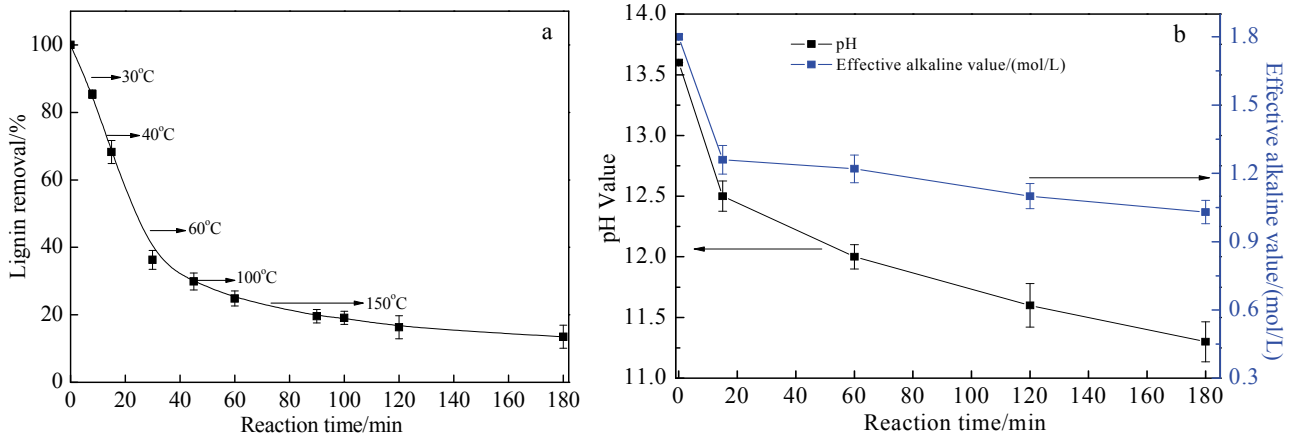

Figure 1. Changes of lignin in the solid, pH value and effective alkaline value during delignification process.

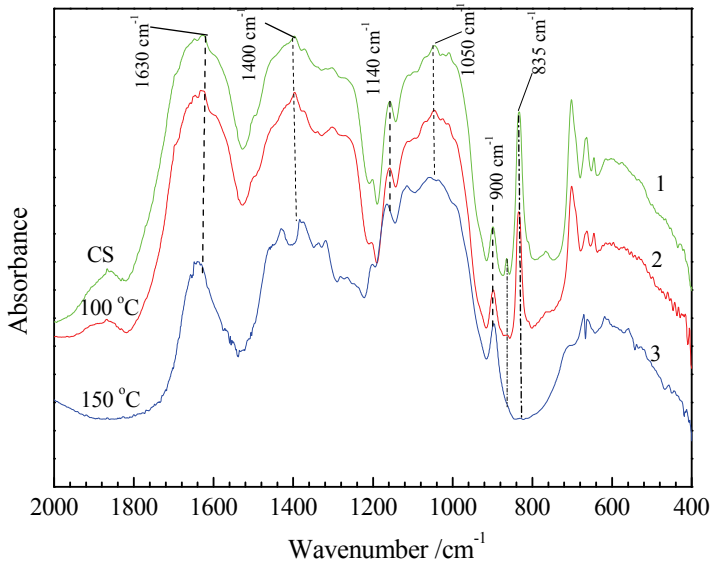

Figure 2. FTIR of corn stover under different delignification temperature, where 1 represents corn stover (CS), 2 represents stover reacted at 100 °C, 3 represents corn stover reacted at 150 °C.

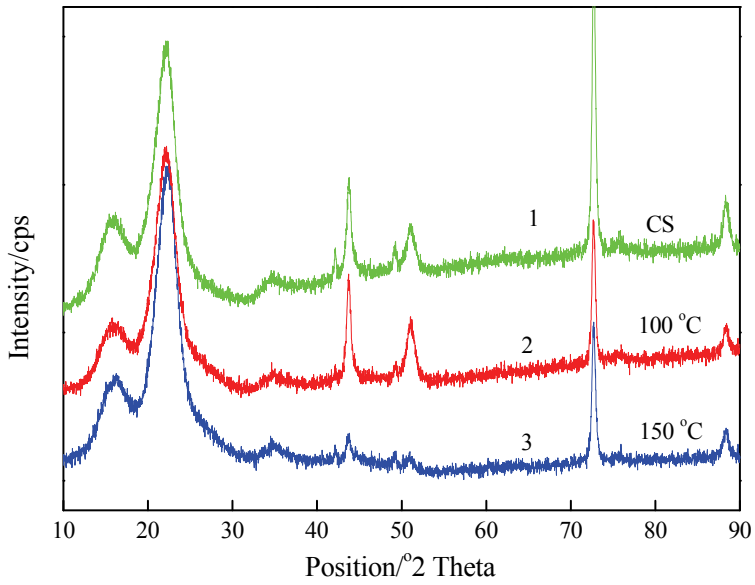

Figure 3. XRD of corn stover at different delignification temperatures, where CS represents corn stover, 2 represents stover reacted at 100 °C, 3 represents corn stover reacted at 150 °C.

where I_c is intensity of crystallite cellulose in the (0,0,2) plane, while I_a is the intensity at 2θ = 19°, which represents the amorphous intensity of the cellulose in crystallite matrix. The result shows that the cellulose in corn stover reacted at 100 and 150 °C is still in crystallite state. With the increase of reaction temperature, the tendency of the increase of the crystallite degree of the cellulose is observed. This result agrees with that of result obtained from FT-IR that the cellulosic crystallite was affected during the reaction. Before reaction, the XRD pattern of corn stover also provides sharp bands from 40 to 80°, which indicates the existence of plant ash such as Si, Al and Ca bonded with organic tissues in corn stover. As the reaction continues, the intensities of those bands begin to decrease even disappear indicating the effective removal of the ash such silica, aluminum oxides etc., during delignification reaction.

After reaction, the prepared paper pulp was characterized. The kappa value of the obtained paper pulp could reach 10, and the tensile and the tear index of paper pulp could reach 50 N m/g and 6 mN m^2/g, respectively. These parameters are comparable to the herbaceous derived paper pulp properties that were prepared by the conventional pulping processes [7].

Kinetics of delignification

Although many studies have been done on delignification of non-wood biomass such as reed, wheat straw, rice straw, etc., the knowledge of kinetics of delignification of corn straw using the combined strong and weak alkaline system are still very limited. Here, the kinetics experiments were conducted under optimized liquid-solid ratio, alkaline amount (KOH, NH_4OH), at 20, 40, 60 and 80 °C. The kinetics of delignification at different temperatures are shown in Figure 4.

The rate of delignification of corn stover could be expressed as:

$$\frac{dL}{dt} = kL^n[OH^{-1}]^m \quad (2)$$

where L represents lignin content in residue in wt.% (on the dry basis), k is reaction rate, n is the order delignification reaction, m is the order of OH^- reaction rate, $[OH^-]$ is the concentration of hydroxide in solution mol/l. Taking a log of both sides gives the expression in the logarithmic form:

$$\ln\frac{dL}{dt} = \ln k + n\ln L + m\ln[OH^-] \quad (3)$$

The experimental results were handled in the multi-variable linear regression by the least square algorithm and the results are shown in Figure 5. All relative variance of the linear surface fitting is over 0.99, indicating a good fit using the logarithmic approximation for kinetic delignification. The activation energy could be determined by Arrhenius law as following:

$$\ln k = \ln k_0 - \frac{E}{RT} \quad (4)$$

All the parameters obtained from surface fitting are summarized in Table 2. The order of reaction of concentration of hydroxide ($[OH]^{-1}$) in solution ranged from 0.33 to 0.44 indicating its order of reaction is between 0.33 and 0.44. In this paper within experimental condition, we assume its reaction is a 0.4 order of the reaction, which is reasonable within our experimental conditions. With respect to lignin reaction, it varies from 0.8 to 1.2 within experimental temperatures. This further proves the fact that delignification reaction of corn stover could be approximately treated as a first order reaction. The activation energy of our result is smaller than that of kraft delignification of wood (120-130 kJ/mol) [13]. This indicates that the lignocellulosic structure of non-wood biomass is generally more porous and readily active than that of wood. According to Kim *et al.* [14], the activation energy of corn stover delignification using lime also reached about 40 kJ/mol, this difference might be due to the different size of the raw materials adopted and strength difference of alkaline between lime and KOH. The activation energy of corn stover using this combined alkaline system is also slightly smaller than those non-wood biomasses using the same combined alkaline system [11], indicating that the corn stover lignin is more readily being removed during the delignification process.

Characterization of black liquor and the acid precipitated lignin

The characteristics of the black liquor obtained are summarized in Table 3. Among many kinds of organic compounds in black liquor, lignin is one of the major components in black liquor. Since the potas-

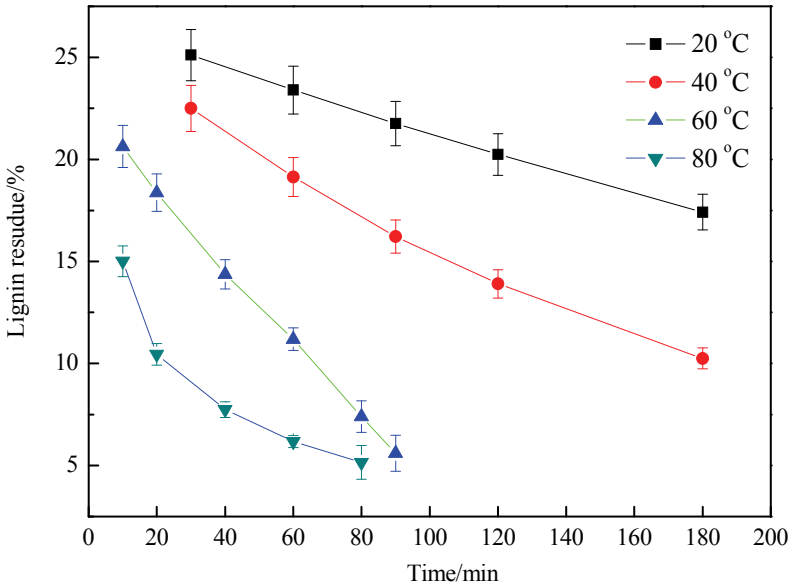

Figure 4. Kinetics of delignification at different temperatures.

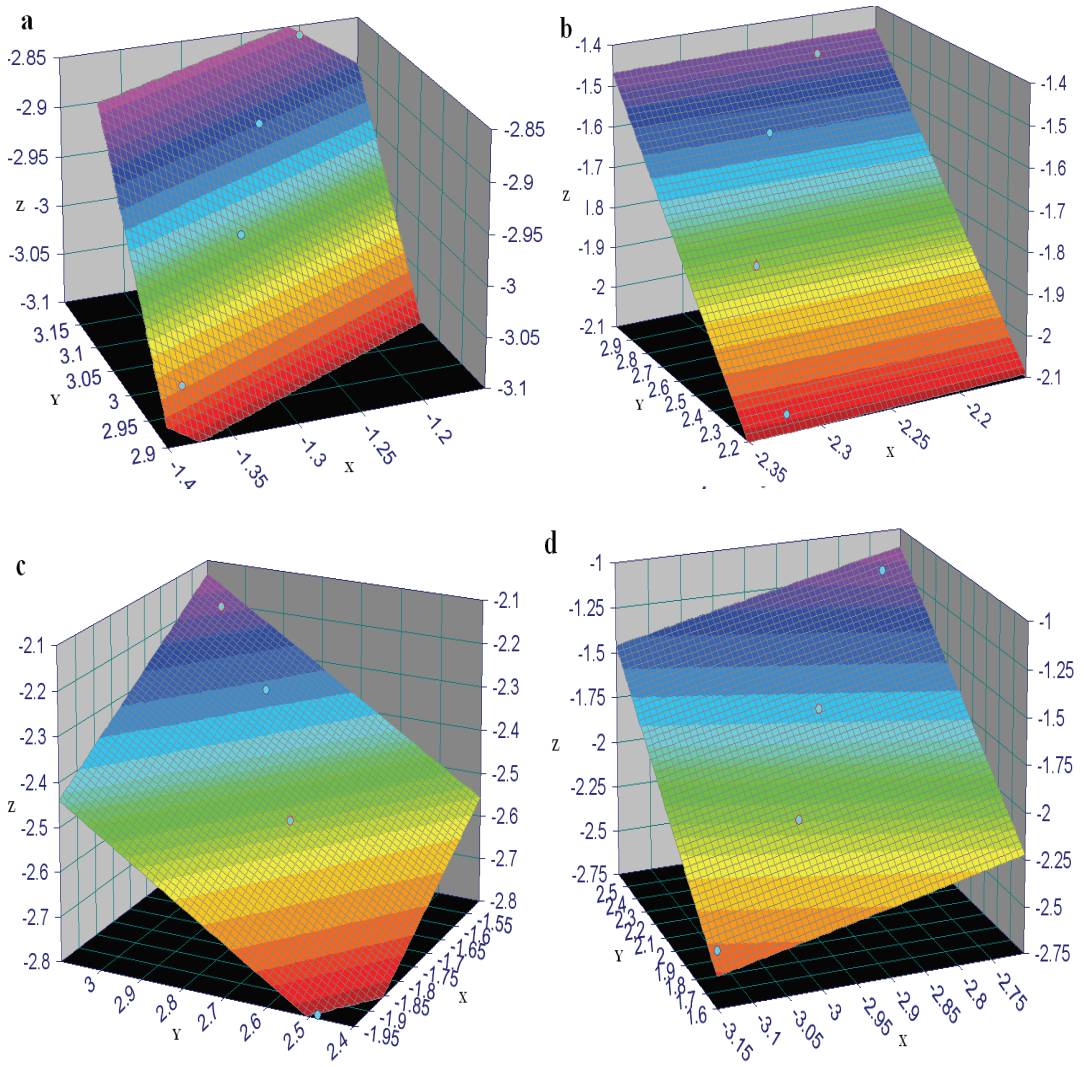

Figure 5. Surface fitting of kinetics of delignification at different temperatures, where a represents 20 °C, b 40 °C, c 60 °C and d 80 °C. X represents log value of [OH]$^{-1}$, Y represents log value of lignin content, whereas Z represents log value of lignin changing rate.

Table 2. Kinetic parameters during delignification

Temperature, °C	*n*	*m*	*k*	*E* kJ/mol	k_0 $L^{0.4}/mol^{0.4}min$	Correlation coefficient
20	0.44	1.2	0.0084	23	400	0.99
40	0.45	0.8	0.0250			
60	0.39	0.8	0.0281			
80	0.33	1.1	0.0726			

sium alkaline and ammonia are applied in this process, the produced black liquor is rich in K and N elements. In order to further increase the added value of black liquor, phosphorous acid was employed to precipitate lignin and thus the remained solution after precipitation simultaneously contained the nutritional element P. By doing this, the acid precipitated lignin and the solution that is rich in N, P, K and organic matter, which is an ideal liquid fertilizer [15], were both obtained. The suspension particle concentration after lignin precipitation could reach about 700 mg/l, which significantly reduces the demand of subsequent AAO (anaerobic-anoxic-oxic) biological sludge treatment. The FT-IR spectra of lignin precipitated under different pH is showed in Figure 6. The spectra of precipitated lignin present bands at 1600, 1510, 1420 and 835 cm^{-1}, indicating that the *p*-coumaryl, coniferyl, and sinapyl units exist in the macromole-

Table 3. Characterization of black liquor

Property	Value
pH	10
Solid materials, g/L	98
Lignin, g/L	31
Chemical oxygen demand (COD_{Mn}), mg/L	66230
BOD_5	8900
Total nitrogen, g/L	3.8
Total potassium, g/L	7.6

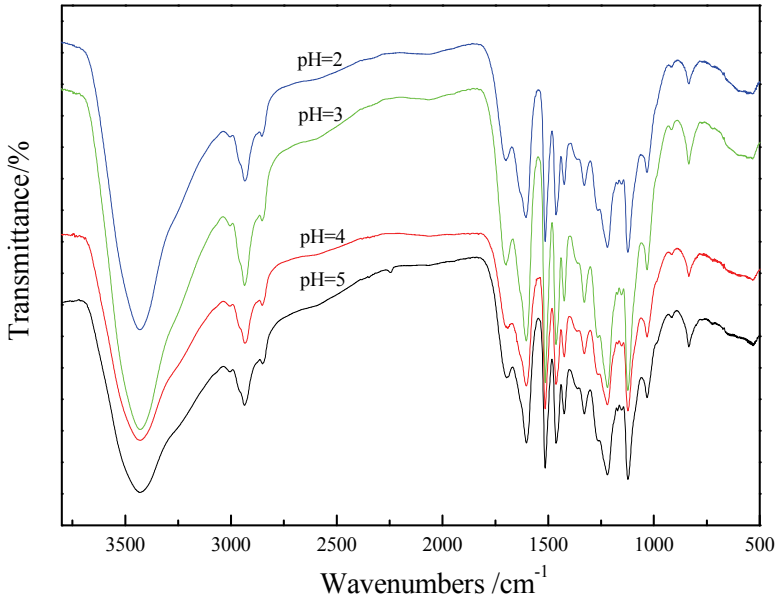

Figure 6. FTIR of lignin precipitated under different pH.

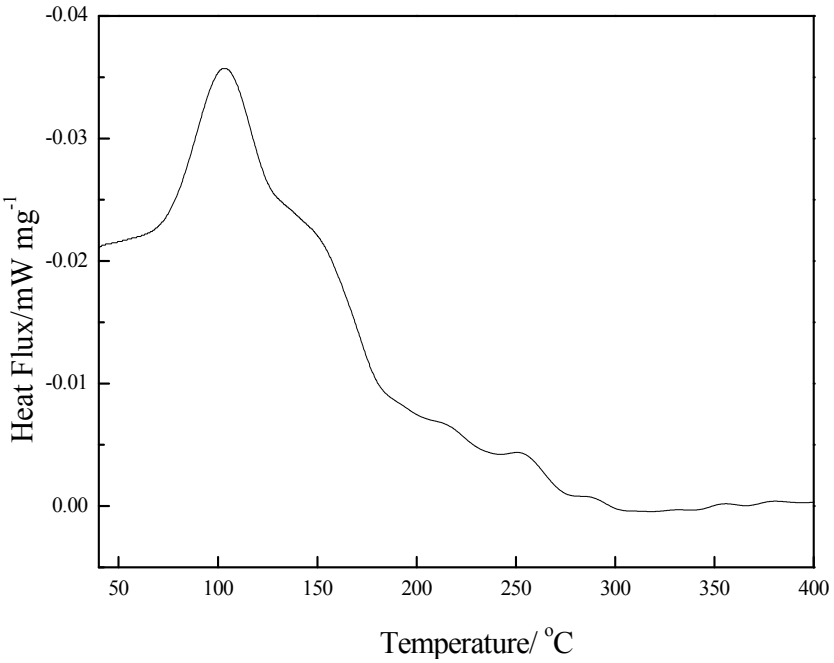

Figure 7. DSC Analysis lignin precipitated at pH 5.

cules matrix. It needs to be addressed that the acid precipitated lignin is different to that of the original lignin that exists in the plant tissue, even though they share the similar phenol structural units such as *p*-coumaryl, coniferyl and sinapyl units. With the decrease of pH, the tendency of the increased transmittance at 1710, which is C=O out plane stretching vibration, is observed. This might be the fact that more C=O functional group were formed during polymerization of acid precipitated lignin.

The lignin precipitated at pH 5 was characterized by GPC, the result show that the weight average, number average molecular mass could reach 2190 and 1560, respectively. The corresponding polydispersity of precipitated lignin could be around 1.4. This result generally agrees with the non-wood acid precipitated lignin [16]. The differential scanning calorimetry (DSC) of acid precipitated lignin at pH 5 is shown in Figure 7. The glass transition of the lignin is observed at around 100 °C, which agrees with results obtained from the alcoholysis lignin [17].

CONCLUSIONS

The self-made KOH together with NH_4OH could effectively remove lignin during delignification reaction. The delignification is composed of three stages: bulk lignin removal (65% removal rate), supplementary lignin removal (85% removal rate) and residue lignin removal (90% removal rate) step, respectively. The *p*-hydroxyl phenol groups in lignin could be completely removed during the delignification reaction. The tendency of the increased crystalline degree of cellulose is observed with increase of reaction temperature. The kinetics of delignification is found to be the first order with respect to remained lignin and 0.4 order with respect to the remained hydroxide concentration. The activation energy of delignification is 23 kJ/mol. The solution obtained from precipitation of lignin is rich in nitrogen, phosphorous, potassium elements and organic matters. The result of GPC shows that the polydispersity of lignin is 1.4. The FT-IR indicates that the *p*-coumaryl, coniferyl and sinapyl units remained in the precipitated lignin matrix.

Acknowledgements

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NAUČNI RAD

ČISTIJA PROIZVODNJA KAŠE KUKURUZNIH ŠUŠKI KORIŠĆENJEM RASTVORA KOH+NH_4OH I KINETIKA NJIHOVE DELIGNIFIKACIJE

U radu je ispitivano dobijanje kaše kukuruznih šuški korišćenjem KOH i NH_4OH. Kombinacijom alkalija lignin se može efektivno izdvojiti tokom dobijanja kaše. Postoje tri faze izdvajanja lignina tokom delignifikacije. Oko 90% lignina se može izdvojiti na temperaturi od 150 °C za 30 min. p-Hidroksil fenolnegrupe lignina se mogu potpuno ukloniti reakcijom delignifikacije. Sa povećenjem reakcione temperature zapaža se povećanje stepen kristalnosti celuloze. Kinetika delignifikacije je prvog reda u odnosu na lignin i 0,4 reda u odnosu na koncentraciju hidroksida. Aktivaciona energija delignifikacije iznosi 23 kJ/mol. Rastvor dobijen posle taloženja lignina je bogat azotom, fosforom, kalijumom i organskim materijama. Kiselo staložen lignin je okarakterisan različitim tehnikama, uključujući FT-IR, GPC I DSC. Rezultati pokazuju da lignin polidisperznosti 1,4 zadržava p-kumaril, koniferil i sinapil jedinice u matrici.

Ključne reči: KOH+NH_4OH, kukuruzne šuške, dobijanje kaše, kinetika, lignin.