Optimization of Pretreatment and Alkaline Cooking of Wheat Straw on its Pulpability Using Response Surface Methodology

Jinpeng Li, Bin Wang,* Kefu Chen, Xiaojun Tian, Jinsong Zeng,* Jun Xu, and Wenhua Gao

The dissolution rates of the chemical compositions of alcohol-benzene extractables (ABE), holocellulose, hemicellulose, and lignin in wheat straw (WS) under different pretreatment conditions were investigated. The individual and interactive effects of three independent parameters, namely, sodium hydroxide (NaOH) dosage (x_1: 8 wt.% to 12 wt.%), sodium sulfide (Na_2S) dosage (x_2: 10 wt.% to 18 wt.%), and time to maximum temperature (x_3: 100 min to 140 min) on screened yield, Kappa number, and brightness of wheat straw pulp (WSP) were analyzed *via* response surface methodology (RSM). The results suggested that the quadratic equations were in good agreement with the experimental figures in the present work. The relative errors of verification results were less than 5%, which indicated that the selected model for explaining the relationship between the variables and the responses was correct. In addition, the relationships between the screened yield, reject yield, brightness, and Kappa number were described and explained. Wheat straw pulpability was optimized in this study *via* RSM.

Keywords: Alkaline cooking; Wheat straw; Pulpability; Response surface methodology

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INTRODUCTION

Wheat straw is one of the most abundant agricultural straws in the world, of which the total production was approximately 9.31×10^{11} kg in 2014 (Bhattarai *et al.* 2015). However, most of the wheat straw in China was directly burnt; only a small fraction was used in the papermaking industry, animal feed industry, and fertilizer industry (Qiu *et al.* 2017). The paper and pulp making industry consumes 100 to 250 m^3 of fresh water per ton of product (Sridhar *et al*. 2012). The black liquor is a mixture of organic and inorganic materials from the pulping process. The production of black liquor has been approximately 500 million tonnes every year around the word (Dafinov *et al*. 2005; Huang *et al*. 2007). As raw material, using agricultural straws clean pulping technology can be regarded as a promising approach to reduce wood consumption (Wan *et al*. 2004; Luis *et al.* 2008).

Pretreatment technology of lignocellulosics can effectively enhance the pulping properties because it can disrupt the tissue structures and increase the available surface area (Sun *et al*. 2002; McIntosh and Vancov 2011; Merali *et al.* 2015). The pretreatment process not only can reduce the pentosan content in the raw material, but it also can remove the organic extracts, ash, acid-soluble lignin, and low molecular carbohydrates in straws (Wang *et al.* 2016; Carvalho *et al*. 2016; Smit and Huijgen 2017). Various pretreatment methods, including chemical, mechanical, thermal, ultrasonic, and enzymatic have been reported (Qi *et al.* 2009; Lin *et al.* 2010; Erdei *et al.* 2013; Song and Zhang 2015; Xing *et*

al. 2016). However, there are several shortcomings such as cost, infrastructure needs, and technological impasses (Antizar-Ladislao and Turrion-Gomez 2010). Alkali-based pretreatment is generally regarded as a preferred method due to its shorter pretreatment time and higher efficiency (Zheng *et al.* 2009; Peng *et al.* 2011a), so the sodium hydroxide (NaOH) often has been used as the alkaline source (Carvalho *et al.* 2016). Treatment of lignocellulosic biomass in alkaline solutions is the best approach to deconstruct ester bonds between carbohydrates and lignin and to dissolve the inorganic compounds, *i.e.* the ash content (Dien *et al.* 2015; Phuong *et al.* 2017). It provides a better way for improving the efficiency of delignification and carbohydrates degradation in the cooking process (Wang *et al.* 2016).

From previous literature, most researchers successfully used chemical pretreatment on wheat straw or committed to the exploration of the cooking procedure (Leponiemi *et al.* 2010; Han *et al.* 2012; Akpinar and Usal 2015). However, limited research has focused on the development of a model for pulpability. Response surface methodology (RSM) is a collection of mathematical and statistical techniques that was first proposed by Box and Wilson in 1951 (Chukwu and Yakubu 2012). It is an efficient way for modeling and analyzing the performance of complex systems (Rastogi and Rashmi 1999; Sridhar *et al.* 2012). Variables of factors could be chosen and designed to determine and simultaneously solve multivariate equations (Rastogi and Rashmi 1999; Cheng *et al.* 2014). The RSM has been widely used for the optimization of various processes in food chemistry, material science, and biotechnology (Wang *et al.* 2011; Borges *et al.* 2016; Gupta *et al.* 2017; Muhammad *et al.* 2017).

In the present work, the dissolution rates of components in WS under different pretreatment conditions were evaluated. The RSM was employed to evaluate the individual and interactive effects of three independent parameters, namely sodium hydroxide (NaOH) (x_1), sodium sulfide (Na_2S) (x_2), and time to maximum temperature (x_3) on screened yield, Kappa number, and brightness of wheat straw pulp (WSP). In addition, the relationships between screened yield, reject yield, brightness, and Kappa number were described and explained. The novel optimization strategy used for the pretreatment and cooking process of wheat straw in this study was expected to provide valuable information for papermaking industry and other fields.

EXPERIMENTAL

Materials

The wheat straw used in this work was provided by Shandong Tranlin Group Co., Ltd. (Shandong, China). The contents of holocellulose, hemicellulose, and lignin of wheat straw used in the present work were 70.3%, 24.2%, and 21.2%, respectively. The details of preliminary treatment on the wheat straw, such as cutting, screening, and cleaning, were described in the authors' previous work (Tian *et al.* 2017). Sodium hydroxide (NaOH; AR, purity ≥ 96.0 wt.%), sodium sulphide (Na_2S; AR, purity ≥ 96.0 wt.%), sodium chlorite ($NaClO_2$, AR, purity ≥ 99.0 wt.%), acetic acid (AR, purity ≥ 99.8 wt.%), sulphuric acid (H_2SO_4, AR, purity ≥ 98.0 wt.%), and ethyl alcohol (AR, purity ≥ 99.5 wt.%) were purchased from Tianjin Kermel Reagent Co. Ltd., Tianjin, China.

Water (18.2 MΩ) was purified with a Millipore Milli-Q system (Millipore Direct-Q5, Billerica, MA, USA).

Pretreatment process

The pretreatment process was performed in an electric oil bath. Then, 5.0 g of the dry wheat straw was placed in a 200-mL Erlenmeyer flask under the desired pretreatment conditions at the ratio of solid to liquid of 1:10. After the pretreatment, the sediment was filtered through glass-filter and washed with distilled water to neutral. The residue was dried in an oven at 105 °C to constant weight and then weighed in an analytical balance. The dry mass loss before and after the pretreatment of the straw was used to calculate the dissolution rate.

Methods

Determination of chemical compositions

The determination of holocellulose, hemicellulose, and lignin (acid insoluble lignin) were according to previous reported methods (Peng *et al.* 2011b; Cao *et al*. 2014). Wheat straw was first ground, and then filtered through an 80-mesh screen. The powder was collected for subsequent experimentation. The wheat straw powder was dewaxed by refluxing with toluene-ethanol (2:1, v/v) in a Soxhlet apparatus for 6 h (Cao *et al*. 2014). Holocellulose was obtained by delignification of wheat straw with 15 wt.% sodium chlorite in acetic acid solution (pH 4-4.2) at 75 °C for 2 h (Nguila *et al*. 2007). The sediment was filtered through a glass-filter and washed with distilled water to pH 7. Then the residue was dried at 105 °C until constant weight. Hemicellulose was isolated using 10% KOH at 25 °C for 10 h with a solid to liquor ratio of 1:20. The content of lignin was determined by TAPPI T 222 method (Ioelovich 2015). Approximately 0.1 g of dewaxed samples were loaded with 10g of H_2SO_4 (72 *wt.* %) at 20 °C for 2 h. The solution was the diluted to a concentration of 3 wt.%, and refluxed for 4 h. After standing overnight, the insoluble residue was filtered through a glass-filter and washed with hot water until it reached pH 7. The residue was dried at 105 °C to constant weight.

Alkaline cooking process design

The pretreated wheat straw was loaded in a digester with a liquid/solid ratio of 10:1 (w/w). The added proportion of sodium hydroxide and sodium sulphide (based on oven-dried raw material) is listed in Table 1. The digester was sealed and heated to 155 °C within a certain time. The response surface design with 3 factors at 3 levels was employed using Design-Expert 8.0.6 (Trial version, State-East, Minneapolis, MN, USA). The parameters and the operating ranges covered are given in Table 1. Dosages of NaOH, dosages of Na_2S and time to maximum temperature were referred to by uncoded variables as x_1, x_2, x_3, respectively. Each independent variable was coded between -1 and +1 in the ranges determined by the preliminary experiment.

Table 1. Coded Independent Variables Used in RSM Design

Factors	Variable	Level		
		-1	0	1
x_1	NaOH (%, Na_2O)	8	10	12
x_2	Na_2S (%, Na_2O)	10	14	18
x_3	Time to maximum temperature (min)	100	120	140

A polynomial regression method was used to fit the experimental data by a quadratic equation using statistical software (Design-Expert 8.0.6). The second order polynomial equation can be expressed as (Sridhar *et al.* 2012),

$$Y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i} \sum_{<j=2}^{k} \beta_{ij} x_i x_j + e_i \quad (1)$$

where Y is the response, x_i and x_j are variables (i and j range from 1 to k), β_0 is the model intercept coefficient, β_j, β_{jj}, and β_{ij} are interaction coefficients of linear, quadratic, and the second-order terms, respectively, k is the number of independent parameters (k = 3), and e_i is the error (Singh *et al.* 2008; Güven *et al.* 2009).

Pulp property measurement

Kappa numbers of the obtained pulps were determined according to ISO 302 (2004). Wheat straw screened pulp (WSSP) was obtained by collecting the filtration which can pass a sieve with 0.20 to 0.25 mm slots. And the remnants were recorded as reject pulp. The dry mass percentage of screened pulp and reject pulp against the wheat straw raw material are the screened yield (%) and reject yield (%), respectively. Brightness was measured by a digital brightness meter (Elrepho 070, Lorentzen, Sweden) equipped with a xenon lamp according to the D65 standard illuminant at a constant temperature (23 °C ± 1 °C) and humidity condition (53% ± 1%). Each sample was evaluated five times and the averaged data was recorded.

RESULTS AND DISCUSSION

Single Conditional Pretreatment

The degree of solubilization of various components from wheat straw in pretreatments depended upon the processing temperature and time and different concentrations of NaOH and Na_2S. Figure 1(a) shows the dissolution rate of the components with different temperatures in hot water. It was revealed that the alcohol-benzene extractive and hemicellulose were more easily dissolved in hot water. The partial dissolution of lignin and hemicellulose in wheat straw could cause more cellulose to be exposed and increase the degradation probability of cellulose, which was the primary reason for the increased dissolution of holocellulose (Qiu *et al.* 2017). When the temperature exceeded 80 °C, the dissolved rate of the holocellulose accelerated. This meant that the holocellulose had begun to decompose at this temperature. Therefore, 80 °C was selected as the pretreatment temperature.

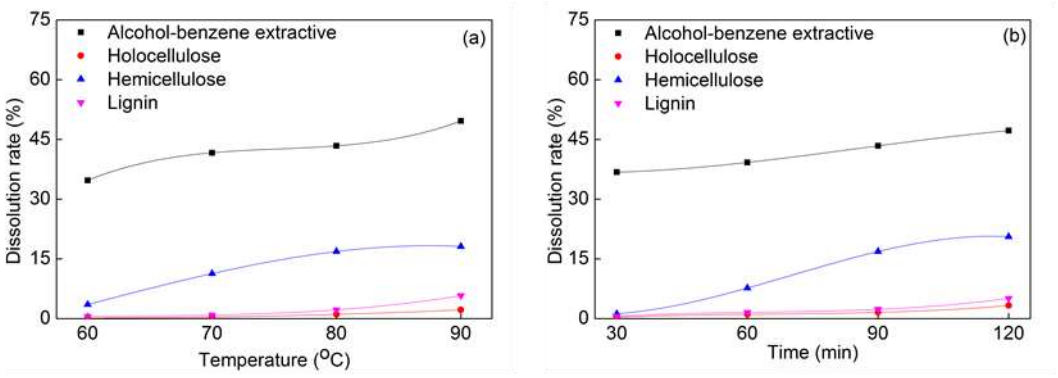

Fig. 1. Effect of pretreatment temperature (liquid/solid ratio of 10:1; *t*=90 min) and time (liquid/solid ratio of 10:1; *T*=80 °C) on the dissolution of chemical components in water

The effects of different time on the components were investigated at 80 °C and the results are shown in Fig. 1(b). The dissolution rate of ABE increased with the increase of time, and the curve tended to be stable at 60 min to 120 min. In addition, increasing pretreatment time exacerbated the hydrolysis of cellulose, which can be seen from the dramatic increase in the results of the dissolution of chemical components after 90 min. This was attributed to the gradual dissolution of carbohydrates in lignocellulosic biomass in hot water, and to the solubilization of hemicellulose to oligomers (Mai *et al*. 2009). To protect the cellulose from excessive hydrolysis and obtain a short treatment time, 30 min was selected as the ideal pretreatment time.

The dissolution rates of the components at different concentrations of NaOH and Na_2S are shown in Fig. 2. The results illustrated that the dissolution of holocellulose and hemicellulose increased with the increase of NaOH dosage, especially when the NaOH concentration was more than 1.0 %. After dissolving out of ABE and lignin, the wheat straw became fluffy because the natural barrier had been destroyed. Due to the increase in the contact area of cellulose, hemicellulose, and alkaline, the hydrolysis of cellulose and hemicellulose increased. Moreover, the lignin dissolution rate gradually increased with the increase of Na_2S dosage. This is attributed to the higher electronegativity and stronger nucleophilic ability of HS^-, which is beneficial to the removal of lignin (Chakar *et al*. 2004). The decreased content of the holocellulose in raw materials was related to the alkalinous Na_2S solution, which improved the hydrolysis of cellulose and hemicellulose (Phuong *et al*. 2017).

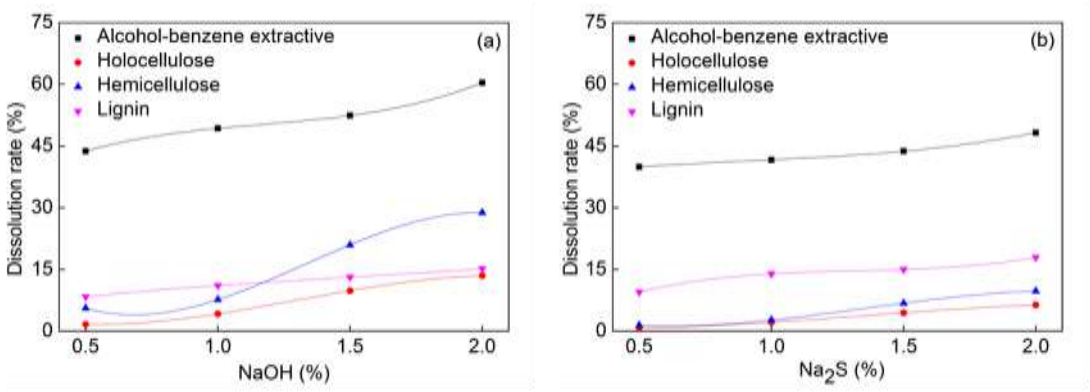

Fig. 2. Effect of NaOH (liquid/solid ratio of 10:1; *t* = 30 min; *T* = 80 °C) and Na_2S (liquid/solid ratio of 10:1; *t* = 30 min; *T* = 80 °C) concentrations on the dissolution of chemical components

NaOH and Na_2S Combined Pretreatment

Figure 3 shows the varieties of ABE, hemicellulose, holocellulose, and lignin in wheat straw under NaOH and Na_2S combined pretreatment. At the same concentration of NaOH, increasing the charge of Na_2S could accelerate the dissolution of lignin. This was due to the β-proton elimination reaction and β-formaldehyde elimination reaction of the β-aryl ether in the main structure of lignin under the alkalinity environment (Tian *et al*. 2017). The HS^- has a stronger nucleophilic attack ability for lignin units, which could prompt the formation of episulfide in lignin units and accelerate the breakage of β-aryl ether bonds and the dissolution of lignin.

Compared with the hot water pretreatment, alkaline cooking tends to be more complicated because all polysaccharide components suffer degradation and hence, detailed studies should be conducted. Early work has confirmed that uronic acid and mannose in hemicellulose could be dissolved rapidly at 100 °C (Vena *et al*. 2013). Appropriately,

increasing alkaline concentration was conducive to the dissolution of hemicellulose and low polymerization of cellulose, and also to the swelling of cellulose (Wu *et al*. 2010). However, using an excessive dosage of NaOH and Na_2S could cause a serious degradation of the raw materials (Han *et al.* 2012). The dissolution rate of C-5 was significantly higher than that of C-1. However, only a small amount of polysaccharides dissolved out in C-1. The selected C-1 pretreatment removed 10.1% of lignin and retained 98.0% of holocellulose, which avoided excessive degradation of carbohydrates in wheat straw. Therefore, C-1 was determined as the optimal pretreatment condition in the present work (0.5 % of NaOH and 0.5 % of Na_2S at 80 °C for 30 min). Overall, alkaline pretreatment successfully delignifies lignocellulose by disrupting the ester bonds cross-linking lignin and xylan (McIntosh and Vancov 2011).

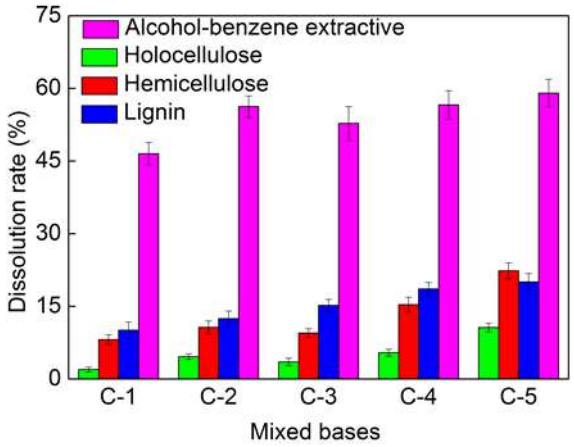

Fig. 3. Effect of NaOH and Na_2S combined pretreatment on the dissolution of chemical components (liquid/solid ratio of 10:1; t = 30 min; T = 80 °C)

Response Surface Analysis

The RSM experiments were performed, and the results Y (response) of screened yield, Kappa number, and brightness were measured. Linear, interactive, quadratic, and cubic models were fitted to the experimental data to obtain the regression equations and are listed in Tables 2 and 3. Sequential model sum of squares (SMSS) was calculated by selecting the highest order polynomial, where the additional terms were significant and the model was not aliased. Model summary statistics (MSS) depended on the model maximizing the adjusted R^2 and the predicted R^2. Both SMSS and MSS were executed to analyze screened yield, Kappa number, and brightness of pulps, and the results are given in Tables 2 and 3 (Sridhar *et al*. 2012). The values (Prob > F) less than 0.0001 indicated the significant of model term (Kim *et al*. 2016). For linear models, Prob > F values (> 0.1000) indicated that the model terms were not significant. In addition, the low adjusted R^2 and predicted R^2 values showed that the models obtained were insignificant. The cubic model was found to be aliased and could not be used for further modeling of experimental data. The quadratic model was chosen for further analysis because it exhibited low Prob > F values (< 0.0500) and high correlation coefficient values.

The quadratic equation with interaction terms was used to fit the experimental data and to identify the relevant model terms. The significance of the second-order model was estimated using an analysis of variance (ANOVA) and the results were presented in Table 4. The final equations obtained in terms of each variable for screened yield (Y_1), Kappa number (Y_2), and brightness (Y_3) are calculated using the following equations:

$$Y_1=45.21-0.63x_1+0.82x_2+1.18x_3+1.00x_1x_2-0.12x_1x_3-2.86x_2x_3-2.96x_1^2-1.71x_2^2-0.30x_3^2 \quad (2)$$

$$Y_2=19.29-0.88x_1+1.93x_2-0.17x_3-1.03x_1x_2-0.31x_1x_3+ 1.09x_2x_3-1.04x_1^2-3.42x_2^2-2.67x_3^2 \quad (3)$$

$$Y_3= 35.57+1.81x_1+1.20x_2-0.31x_3-0.32x_1x_2+1.10x_1x_3-0.27x_2x_3+2.99x_1^2+4.77x_2^2+3.74x_3^2 \quad (4)$$

Table 2. Sequential Model Sum of Squares for Screened Yield, Kappa Number, and Brightness

Source	Sum of Squares	Degrees of Freedom	Mean Square	F Value	Prob > F	Remark
Sequential Model Sum of Squares for Screened Yield						
Mean	31247.51	1	31247.51			
Linear	19.77	3	6.59	0.94	0.4496	
2F1	36.79	3	12.26	2.26	0.1442	
Quadratic	53.00	3	17.67	92.58	< 0.0001	Suggested
Cube	1.27	3	0.42	24.53	0.0049	Aliased
Residual	0.069	4	0.017			
Total	31358.41	17	1844.61			
Sequential Model Sum of Squares for Kappa Number						
Mean	4318.15	1	4318.15			
Linear	36.41	3	12.14	1.46	0.2704	
2F1	9.37	3	3.12	0.32	0.8129	
Quadratic	91.35	3	30.45	29.86	0.0002	Suggested
Cube	6.45	3	2.15	12.50	0.0168	Aliased
Residual	0.69	4	0.17			
Total	4462.42	17	262.50			
Sequential Model Sum of Squares for Brightness						
Mean	28547.49	1	28547.49			
Linear	38.58	3	12.86	0.76	0.5364	
2F1	5.57	3	1.86	0.086	0.9659	
Quadratic	213.73	3	71.24	645.17	< 0.0001	Suggested
Cube	0.67	3	0.22	8.44	0.0333	Aliased
Residual	0.11	4	0.026			
Total	28806.14	17	1694.48			

Lack-of-fit tests were used to evaluate the model adequacy. The results of lack-of-fit tests for the screened yield, Kappa number, and brightness were 0.0049, 0.0168, and 0.0333, respectively. The values were insignificant and indicated that the models matched well with the observed data. The F values of models (63.79, 14.94, and 258.48) implied that most of the variation in the response could be explained by the regression equation (Sridhar *et al.* 2012). The associated Prob > F values were less than 0.0002 for screened yield, Kappa number, and brightness, which illustrated that the terms were significant in the model. The model gave coefficients of determination (R^2) values of 0.9880, 0.9505, and 0.9970 for screened yield, Kappa number, and brightness, respectively. The values of R^2 almost equal to 1.0 were indicated that a high correlation between the experimental

results and the predicted values (Gönen and Köylü 2016). The points of the predicted *versus* experimental plots for screened yield, Kappa number, and brightness were clustered along the diagonal as shown in Fig. 4. The results revealed that the predicted values fitted well with the observed ones.

Table 3. Model Summary Statistics for Screened Yield, Kappa Number, and Brightness

Source	Standard Deviation	Predicted R^2	Adjusted R^2	R^2	PRESS	Remark
Model Summary Statistics for Screened Yield						
Linear	2.65	-0.4817	-0.0114	0.1782	164.32	
2F1	2.33	-0.5261	0.2160	0.5100	169.24	
Quadratic	0.44	0.8162	0.9725	0.9880	20.38	Suggested
Cube	0.13		0.9975	0.9994	+	Aliased
Model Summary Statistics for Kappa Number						
Linear	2.88	-0.1852	0.0798	0.2524	170.99	
2F1	3.14	-0.9289	-0.0923	0.3173	278.28	
Quadratic	1.01	0.2772	0.8869	0.9505	104.28	Suggested
Cube	0.41	-0.1852	0.9809	0.9952	+	Aliased
Model Summary Statistics for Brightness						
Linear	4.11	-0.2348	-0.0472	0.1492	319.39	
2F1	4.63	-0.9904	-0.3269	0.1707	514.81	
Quadratic	0.33	0.9581	0.9932	0.9970	10.84	Suggested
Cube	0.16		0.9984	0.9996	+	Aliased

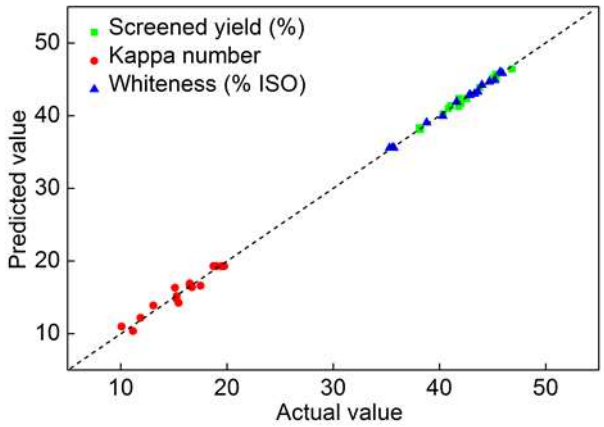

Fig. 4. Comparison of actual and predicted values

Verification Results

To verify the effectiveness of the predicted process parameters, verification experiments were performed. The optimum process conditions, predicted, and verified values for alkaline cooking of pretreated WS are summarized in Table 5.

To obtain the higher screen yield and Kappa values of the WSP, the optimized determination values of 9.62%, 13.36%, and 127 min for charge of NaOH, Na_2S dosage, and time to maximum temperature were selected. The relative errors for screened yield and Kappa number and brightness were 3.65%, 4.43%, and 35.54, respectively. To obtain the higher brightness and low Kappa numbers of the WSP, the responded NaOH dosage, Na_2S dosage, and time to maximum temperature were 13.94 wt.%, 17.96 wt.%, and 100.20 min, respectively.

Table 4. ANOVA of Quadratic Equation for Straw Pulp Properties

Source	Coefficient Estimate	Sum of Squares	DF	Mean Square	F value	Prob > F	Remark
ANOVA of the Quadratic Equation for Screened Yield							
Model Intercept	45.21	109.56	9	12.17	63.79	< 0.0001	Significant
X_1	-0.63	3.23	1	3.23	16.90	0.0045	Significant
X_2	0.82	5.33	1	5.33	27.93	0.0011	Significant
X_3	1.18	11.21	1	11.21	58.74	0.0001	Significant
X_1X_2	1.00	4.02	1	4.02	21.07	0.0025	Significant
X_1X_3	-0.12	0.055	1	0.055	0.29	0.6073	
X_2X_3	-2.86	32.72	1	32.72	171.45	< 0.0001	Significant
X_1^2	-2.96	36.98	1	36.98	193.77	< 0.0001	Significant
X_2^2	-1.71	12.33	1	12.33	64.59	< 0.0001	Significant
X_3^2	-0.30	0.37	1	0.37	1.93	0.2070	
Residual		1.34	7	0.19			
Lack of Fit		1.27	3	0.42	24.53	0.0049	Significant
Pure Error		0.069	4	0.017			
Cor Total		110.90	16				
ANOVA of the Quadratic Equation for Kappa Number							
Model Intercept	19.29	137.13	9	15.24	14.94	0.0009	Significant
X_1	-0.88	6.23	1	6.23	6.11	0.0427	Significant
X_2	-1.94	29.95	1	29.95	29.37	0.0010	Significant
X_3	-0.17	0.22	1	0.22	0.22	0.6532	
X_1X_2	-1.03	4.24	1	4.24	4.16	0.0807	
X_1X_3	-0.31	0.37	1	0.37	0.36	0.5649	
X_2X_3	1.09	4.75	1	4.75	4.66	0.0677	
X_1^2	-1.04	4.52	1	4.52	4.44	0.0732	
X_2^2	-3.42	49.15	1	49.15	48.19	0.0002	Significant
X_3^2	-2.67	29.94	1	29.94	29.36	0.0010	Significant
Residual		7.14	7	1.02			
Lack of Fit		6.45	3	2.15	12.50	0.0168	Significant
Pure Error		0.69	4	0.17			
Cor Total		144.27	16				
ANOVA of the Quadratic Equation for Brightness							
Model Intercept	35.66	257.88	9	28.65	259.48	< 0.0001	Significant
X_1	1.74	26.28	1	26.28	238.00	< 0.0001	Significant
X_2	1.12	11.52	1	11.52	104.32	< 0.0001	Significant
X_3	-0.31	0.78	1	0.78	7.07	0.0325	Significant
X_1X_2	-0.32	0.42	1	0.42	3.83	0.0914	
X_1X_3	1.10	4.84	1	4.84	43.83	0.0003	Significant
X_2X_3	-0.27	0.30	1	0.30	2.74	0.1419	
X_1^2	2.95	37.67	1	37.67	341.11	< 0.0001	Significant
X_2^2	4.72	95.64	1	95.64	866.11	< 0.0001	Significant
X_3^2	3.70	58.93	1	58.93	533.63	< 0.0001	Significant
Residual		0.77	7	0.11			
Lack of Fit		0.67	3	0.22	8.44	0.0333	Significant
Pure Error		0.11	4	0.026			
Cor Total		258.65	16				

Table 5. Optimum Conditions for Alkaline Cooking of Pretreated WSP

Condition [a]	Value	Verification	Screened Yield (%)	Kappa Number	Brightness (% ISO)
High Screen Yield and Kappa Values					
NaOH (wt.%)	9.62	Predicted Value	45.62	19.18	35.54
Na_2S (wt.%)	13.36	Verified Value	47.35	20.07	36.28
t (min)	127.00	Relative Error (%)	3.65	4.43	2.04
High Brightness and Low Kappa Values					
NaOH (wt.%)	13.94	Predicted Value	43.34	7.94	48.92
Na_2S (wt.%)	17.96	Verified Value	42.39	7.78	48.07
t (min)	100.20	Relative Error (%)	2.24	2.06	1.77

The relative error values of 2.68%, 4.66%, and 48.92 for screened yield, Kappa number, and brightness, respectively, indicated that the experimental results were in good correlation with the predicted results. The relative errors between the predicted values of the optimized condition and the actual values were less than 5%, which revealed that the model chosen to explain the relationship between the variables and the responses was correct.

Yield *vs.* Kappa Number

Reject yield represented the uniformity of raw material and the efficiency of chemical treatment (Wan *et al*. 2004). The relationships of the screened yield, the ratio of reject pulp, and Kappa number are shown in Fig. 5. An interesting phenomenon was that the reject yield showed a slight increase with increasing the Kappa number (≤ 17). Most of the reject yields were near to 1%, indicating that the alkaline cooking method of wheat straw was relatively efficient (Masrol *et al*. 2017). However, it seemed that the Kappa number at 17 was a point of inflection of screened yield.

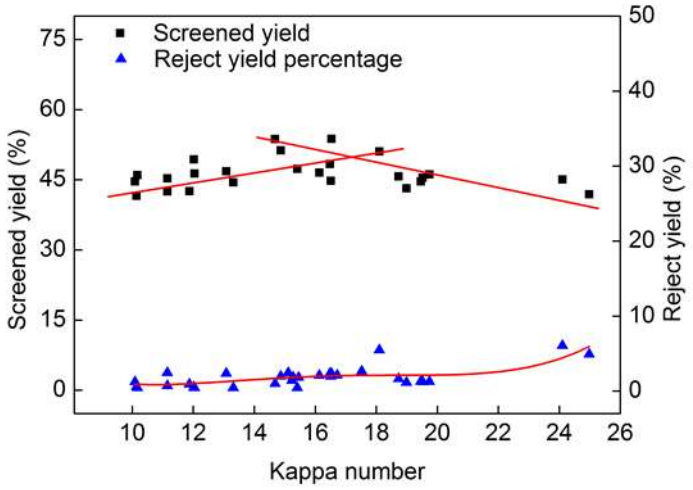

Fig. 5. Relationship among Kappa number and screened yield and reject yield of WSP

When subjected to prolong pulping time, wheat straw fibers would undergo more penetration, diffusion and chemical attack due to its porosity and lower density (Deniz *et al*. 2004). Previous work has been established that longer time to maximum temperature was contributed to a better delignification. But it was also found that yield and viscosity of pulps decreased greatly by extending cooking time (GüMüŞKaya *et al*. 2006).

Brightness *vs.* Kappa Number

The cooking process is mainly a delignification process. The lignin macromolecule is mainly composed of phenyl propane structures (Jeong *et al.* 2013). Many chromophoric groups are present the molecule, such as phenolic hydroxyl, quinone structures, and carbonyl (Fjellström *et al*. 2008). In the appropriate condition, the reactions between the chromophore groups and the chromophoric groups caused a discoloration of the pulp (Narvestad *et al.* 2013). The relationship between the Kappa number and brightness of WSP is described in Fig. 6. It is noted that the brightness of WSP decreased with the rising Kappa values. A high Kappa number meant that the pulps contained more chromophoric groups and caused a lower value of brightness.

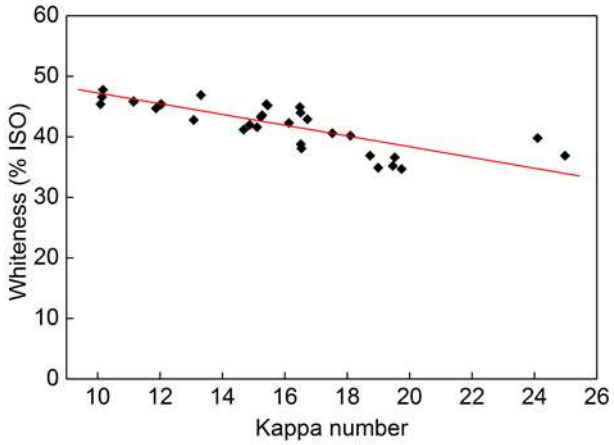

Fig. 6. Relationship between Kappa number and brightness of WSP

CONCLUSIONS

1. The selected pretreatment of NaOH (0.5 %) and Na_2S (0.5%) at 80 °C for 30 min removed 10.1% of lignin and retained 98.0% of holocellulose in wheat straw, which avoided excessive decomposition of carbohydrates.
2. The quadratic model showed more accuracy in the presentwork. The NaOH dosage, Na_2S dosage, and time to maximum temperature were important factors that influenced the pulpability. The relative errors between the predicted values and the actual experimental values were less than 5%, which confirmed that the selected model for explaining the relationship between the variables and the responses was correct.
3. Increasing the Kappa number, the screened yield first increased and then decreased, and the pulp brightness decreased.

ACKNOWLEDGMENTS

The authors are grateful for the support of the China Postdoctoral Science Foundation (2017T100633 and 2016M602472), the National Natural Science Foundation of China (31600471), the Natural Science Foundation of Guangdong Province (2015A030310369 and 2015A030313221), the Fundamental Research Funds for the Central Universities (2017MS087 and 2017ZD089), 111 Plan and Guangdong Provincial

Science and Technology Plan Projects (No.: 2015B020241001, Name: Research and Application of Biomass Pretreatment and Ethanol Production Technology), and the financial support of Science and Technology Plan Projects of Guangzhou city (Number: 201504010013, Name: Study on Quality Intelligent Control of Modern Paper Machine and Energy-saving Technology with Equipment).

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Article submitted: July 20, 2017; Peer review completed: October 14, 2017; Revised version received and accepted: October 28, 2017; Published: November 2, 2017.
DOI: 10.15376/biores.13.1.27-42