Optimization of Selective Acid Hydrolysis of Cellulose for Microcrystalline Cellulose using $FeCl_3$

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In the process of acid hydrolysis of cellulose, hydrolyzing the amorphous regions while retaining the crystalline regions is the key technology for obtaining microcrystalline cellulose products. This paper investigated the influence of $FeCl_3$ on selective acid hydrolysis of crystalline regions and amorphous regions of cellulose. X-ray diffraction data indicated that $FeCl_3$ can enhance the selectivity of acid hydrolysis for amorphous regions of cellulose, thus improving the crystallinity of hydrocellulose. Meanwhile, the crystalline structure did not change. Response surface methodology (RSM) was employed to optimize the crystallinity of hydrocellulose with respect to $FeCl_3$ concentration, HCl concentration, reaction time, and temperature, and the relevant mathematical regression equation model was established. Under optimal conditions, the crystallinity of hydrocellulose was as high as 63.59% at 88.28 °C, 2.46 M HCl, 0.4 M $FeCl_3$, and reaction duration of 64.02 min, which was in agreement with the predicted value.

Keywords: Microcrystalline cellulose; Amorphous regions; Hydrocellulose; Metal ions; Response surface methodology

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INTRODUCTION

Microcrystalline cellulose (MCC) is a type of structural material made from natural cellulose that has been hydrolyzed by inorganic acid or by enzymolysis. Acid hydrolysis is the predominant method for industrial microcrystalline production because of the lower price and higher degree of crystallinity compared to that obtained from enzymes (Adel *et al.* 2011; Hanna *et al.* 2001; Lee *et al.* 2009). It is a highly flowable particulate material having a short rod or granular structure, and is odourless and tasteless. The degree of polymerization of MCC is usually lower than 350, and the average particle size is between 20 and 40 μm (Abd-Allah *et al*. 2009). Due to the special characteristics of insolubility in water, dilute acid, and organic solvents as well as great hygroscopicity, MCC has been widely used in pharmaceuticals, foods, and chemicals (daily and industrial) (Uesu *et al.* 2000).

The raw material sources for MCC are predominantly wood fiber and cotton fiber. Considering the production costs and other issues, other non-wood raw materials such as soybean, bagasse, corn stalk, rice husk, peanut shell, and other agricultural wastes have also aroused attention as potential MCC sources in recent years (Adel and El-Shinnawy 2012; Okhamafe *et al.* 1995). Because of differences in the natural aggregation structures of crystalline and amorphous regions, the crystalline regions from high purity cellulose are used in the production of MCC, which is a high value-added product. However, current technologies have a poor selectivity between amorphous and crystalline regions in the process of acid hydrolysis, resulting in low yields and poor product properties, especially in the case of MCC made from non-wood raw materials (Abd-Allah *et al*. 2009). Meanwhile, the hydrolysate from amorphous regions is discarded, resulting in a lot of waste. Therefore, a method to promote the degradation of the amorphous regions by acid hydrolysis while retaining crystalline regions as much as possible is essential to MCC production. Moreover, improving the selectivity of the amorphous regions and realizing the "Orientation" hydrolysis of cellulose can allow a significant improvement on the yield and crystallinity of the MCC.

Metal inorganic salts as catalysts for enhancing the hydrolysis efficiency of cellulose has been demonstrated by many researchers. Nguyen and Tucker (2002) found that a small amount of $FeSO_4$ can significantly improve the reducing sugar content of the cellulose hydrolysis liquid of coniferous sawdust, while the hydrolysis efficiency of cellulose can be enhanced in the presence of Fe^{3+} and H^+ (Ren *et al.* 2012). Recently, Kamireddy *et al.* (2013) reported the mechanism of cellulose degradation by inorganic metal salts such as $FeCl_3$, $CuCl_2$, and $AlCl_3$. However, many researchers have focused primarily on the preparation of MCC using different raw materials, so the reports on the efficient promotion of cellulose selective acid hydrolysis by metal ions for MCC preparation are limited. To enhance the selectivity of acid hydrolysis in cellulose amorphous regions, this study focused on the methods and mechanism of transition metal ion assisted catalytic acid hydrolysis with the purpose of obtaining a higher degree of hydrolycellulose crystallinity.

The response surface method (RSM) is an empirical modeling technique derived for evaluation of the relationship of a set of multiple variables or factors (Karunanithy and Muthukumarappan 2011). RSM can be used to optimize the selective acid hydrolysis of cellulose for MCC by $FeCl_3$ catalysis. Different parameters affecting crystallinity of hydrocellulose, including $FeCl_3$ concentration, HCl concentration, reaction time, and temperature were examined. This work was also undertaken to develop a useful tool to predict and optimize the selective hydrolysis process of cellulose, which mainly focused on the effects of inorganic metal salt in the process of hydrolysis for MCC production. The corresponding mathematical regression model equation was used to provide some theoretical guidance for MCC preparation.

EXPERIMENTAL

Materials

Dissolving pulp from *Eucalyptus* sulfate pulp, the raw material for MCC in this study, was received from Shan Dong Pulp & Paper Co., Ltd. (China). The main constituents were α-cellulose (92.26%) and a small amount of hemicelluloses. The brightness was 86.8%ISO and the ash content was 0.08%. The pulp was separated and dewatered by water immersion for 24 h before use. All chemicals (*e.g.*, $FeCl_3{\bullet}6H_2O$, HCl) were of analytical grade and purchased from Beijing Chemical Reagent Co. (China).

Pulp slurry (10 g) in 500 mL three-mouth flasks was treated with varying concentrations of HCl and $FeCl_3$ solution (solid-liquid ratio of 1:15) and stirred at 120 rpm. The flasks were heated to various temperatures and reaction times in a constant temperature water bath. Samples were taken from the reaction mixture under different reaction parameters according to the experimental design (see Table 1). Each sample from the hydrolysis solution was immediately washed with deionized water until the filtrate was at neutral pH. Then the sample was centrifuged to remove the water and air-dried. The obtained products of hydrocellulose were used in subsequent testing.

Central Composite Design (CCD)

On the basis of the single factor experimental results from previous studies (Zhang *et al.* 2012; Li *et al.* 2013), a four-factor three-level response CCD, which required 27 runs (3 replicates of the central runs, 8 stars (2^n), and 16 factorial runs by 2^n, n = 4) was used to optimize the $FeCl_3$ acid hydrolysis of cellulose for MCC. Table 1 shows the range of the independent variables and experiment design levels used in this study.

The four variables and their value range were chosen based on preliminary studies. Three-dimensional surface and contour analysis were applied to investigate and validate the influence of process variables on crystallinity from the hydrolysis of cellulose. $FeCl_3$ concentration (0.2 to 0.4 M), HCl concentration (1.0 to 4.0 M), reaction time (40.0 to 70.0 min), and temperature (65.0 to 90.0 °C) were input parameters; the crystallinity of hydrocellulose was coded R in the statistical analysis as the response value. The factors were coded in levels (-1.546, -1, 0, 1, 1.546) before fitting the model.

Table 1. Coded Values of the Variables for the Central Composite Design

Coded symbol	Variable	Levels				
		-1.546	-1	0	1	1.546
X_1	$FeCl_3$ concentration (M)	0.1	0.2	0.3	0.4	0.5
X_2	HCl concentration (M)	0.2	1.0	2.5	4.0	4.8
X_3	Reaction Time (min)	31.8	40.0	55.0	70.0	78.2
X_4	Temperature (°C)	58.1	65.0	77.5	90.0	96.8

Analytical Methods

The fracture surface morphology of hydrocellulose was characterized with a Hitachi S-4800 (Hitachi, Tokyo, Japan) scanning electron microscope (SEM). The samples were gold coated and analyzed at an accelerating voltage of 3 kV.

The crystalline structure of samples were analyzed by X-ray diffraction (XRD) on a D/max-2200 PC automatic XRD (Rigaku Co. Ltd., Tokyo, Japan) using a Ni-filtered Cu-Kα radiation source (λ =0.1518 nm). The X-ray diffractograms were recorded from 6° to 50° 2θ with a goniometer at a scanning speed of 2°/min. The crystallinity was calculated by the total diffracted area and the area under the crystalline peaks, which were determined by integration after correcting the data for absorption. The ratio of the crystallinity of samples to the standard formless materials was taken as the relative crystallinity, which is represented as follows,

$$C_r = F_c /(F_a + F_c) \times 100\% \quad (1)$$

where C_r is the relative crystallinity, whereas F_a and F_c are the area of noncrystalline and crystal regions, respectively (Sun *et al.* 2008). Each sample was measured at least twice to reduce errors.

Statistical Analysis

The data were analyzed using Design-Expert software 7.1.6 (Stat-Ease, Minneapolis, MN, USA). The mathematical relationship between the response of these variables and the independent variables can be expressed by second-degree quadratic polynomial equation (Qi *et al.* 2009),

$$R = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 \quad (2)$$

where R is the predicted value, b_0 is the constant, X_1 is the $FeCl_3$ concentration, X_2 is the HCl concentration, X_3 is reaction time, X_4 is the temperature, b_0 is the offset term, b_1, b_2, b_3, and b_4 are linear coefficients, b_{12}, b_{13}, b_{14}, b_{23}, b_{24}, and b_{34} are cross-product coefficients, and b_{11}, b_{22}, b_{33}, and b_{44} are quadratic coefficients. The accuracy and general ability of the above polynomial model can be evaluated by the coefficient of determination R^2. Analysis of variance (ANOVA) was employed to determine the interaction effects between the factors, and a quadratic surface plot was generated (Teh *et al.* 2013). The adequacy of the model was tested using ANOVA, a normal probability plot, and a residual plot. An F-test was used to determine the statistical significance of the model and the significance of the regression coefficients.

RESULTS AND DISCUSSION

Effect of $FeCl_3$ Addition on Cellulose Hydrolysis

To determine optimal acid hydrolyzing efficiency, the concentration of $FeCl_3$ varied from 0.1 to 0.4 M, while the concentration of HCl was fixed at 3 M. The hydrolysis temperature and time were set at 90 °C and 55 min, respectively. The relationship of Fe^{3+} concentration, crystallinity, and cellulose yield under these conditions are shown in Fig. 1.

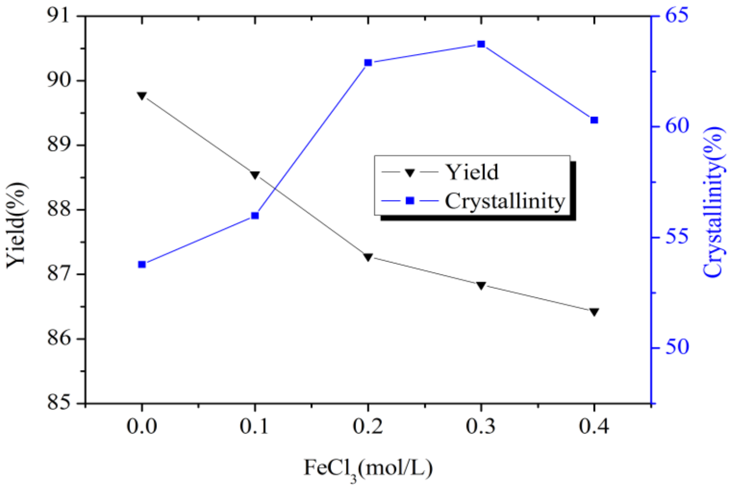


Fig. 1. Effect of $FeCl_3$ dosage on the yield and crystallinity of hydrocellulose

The results in Fig. 1 clearly show that cellulose yield declined and crystallinity increased with increasing $FeCl_3$ concentration. The H^+ can diffuse into the amorphous regions and surfaces of crystalline region and break the intramolecular glycosidic bonds of cellulose. These processes lead to physical swelling along with the chemical degradation of cellulose and result in the decreasing of yield. This phenomenon shows that the addition of metal ions can improve the acid hydrolyzing selectivity of amorphous regions, resulting in an improvement of crystallinity of the hydrolyzed cellulose (Li *et al.* 2010).

A possible explanation is that cellulose in the crystalline region is more difficult to access by the acids due to its crystalline nature and tight structure (Li *et al.* 2013). This difference in cellulose structure determines the selectivity of acid hydrolysis. Metal ions can increase the rate of acid hydrolysis in amorphous regions. Oxygen atoms O_5, and carbon atoms C_2, C_3, and C_6 from the cellulose glucose unit have a higher reaction activity, with oxygen atoms readily adsorbing Fe^{3+} to form an annular intermediate complex which increased the pyranose ring bond angles and bond length, and lowered the activation energy of the reaction (Zhao *et al.* 2011). In addition, the hydrolysis of cellulose is enhanced in acidic solution (Ma *et al.* 2005), as shown in the following balance equation:

$$x\,Fe^{3+} + yH_2O \rightleftharpoons Fe_x(OH)_y^{(3x-y)+} + yH^+ \qquad (3)$$

Fe^{3+} can dissociate into complex ions in aqueous solvent such as water. They form coordinate covalent bond with some water molecules and more H^+ was generated. Due to the increase in H^+ concentration in the reaction system with the increase of Fe^{3+} concentration, H^+ can effectively degrade the glycoside bond between cellulose glucose unit. Hence, the catalyst $FeCl_3$ increased the rate of hydrolysis reaction and provided a high crystallinity of MCC.

SEM Observation

The SEM micrographs of cellulose and hydrocellulose were analyzed to investigate the structure of these fibers (Fig. 2). The samples under the experimental conditions of 0.3 M $FeCl_3$, while the concentration of HCl was fixed at 3 M, and the hydrolysis temperature and time were set at 90 °C and 55 min, respectively. The untreated samples showed an even and smooth surface at low magnification, indicating a rigid and highly ordered surface structure (Fig. 2a).

At a higher magnification, folds and large number of cracks on the fiber surface were apparent, which provided a larger contact area and therefore higher accessibility of cellulose by acid and catalyst (Fig. 2b). Following acid hydrolysis, the fibers were degraded into short, broken fragments (Fig. 2c to Fig. 2d). Also, the degradation of the fiber caused a transverse fracture, and also appeared to have a certain degree of erosion and peeling. The average fiber length was 57 μm. After the addition of $FeCl_3$, the degree of fiber degradation increased and the average length of particles was reduced by up to 48 μm (Fig. 2e and Fig. 2f).

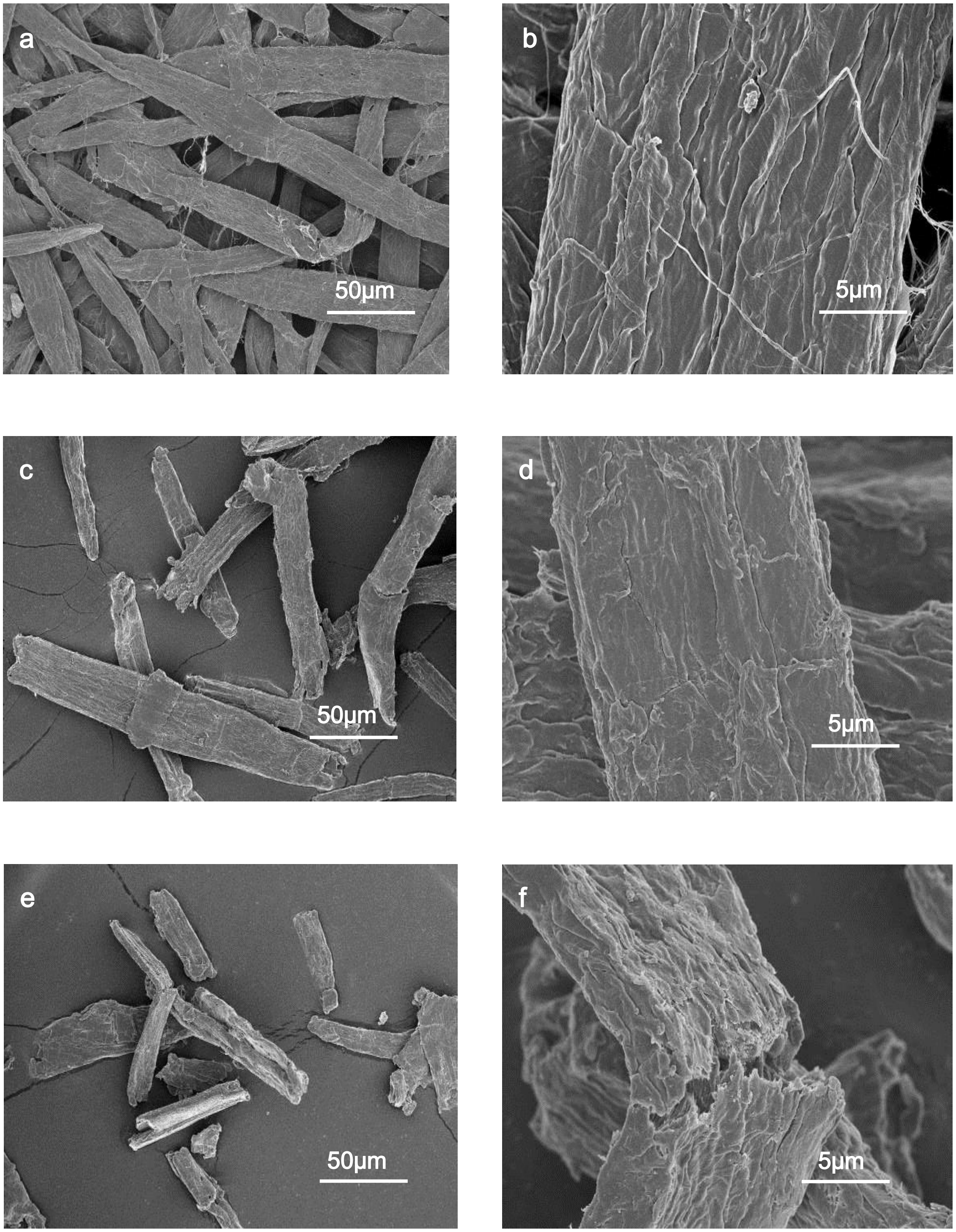


Fig. 2. SEM micrographs of (a, b) normal cellulose (c, d) hydrocellulose fibers, and (e, f) hydrocellulose fibers treated with 0.3 M $FeCl_3$

XRD Analysis

As shown in Fig. 3, the characteristic X-ray diffraction pattern of all diffractograms showed the typical crystalline structure of native cellulose or cellulose I. As indicated by the similar curves and peaks in the figure, the whole structure of cellulose was not transformed by acid hydrolysis. But the peak intensity of hydrocellulose was high, at 22.5° of diffraction, and the dispersion peak intensity of the amorphous portion was relatively low, near 18°. A possible explanation is that the glycosidic bond from amorphous regions was partially degraded and cleaved in the process of hydrolysis, while the well-organized crystalline regions changed little and thus there was an increase in crystallinity. The results show that the crystallinity of hydrocellulose with different treatments were: cellulose raw material, 49.98%; hydrocellulose without $FeCl_3$ treatment, 53.78%; and hydrocellulose with 0.3 M $FeCl_3$ treatment, 63.59%. This provided evidence that $FeCl_3$ can accelerate the selective acid hydrolysis of cellulose and consequently improve the crystallinity of hydrocellulose.

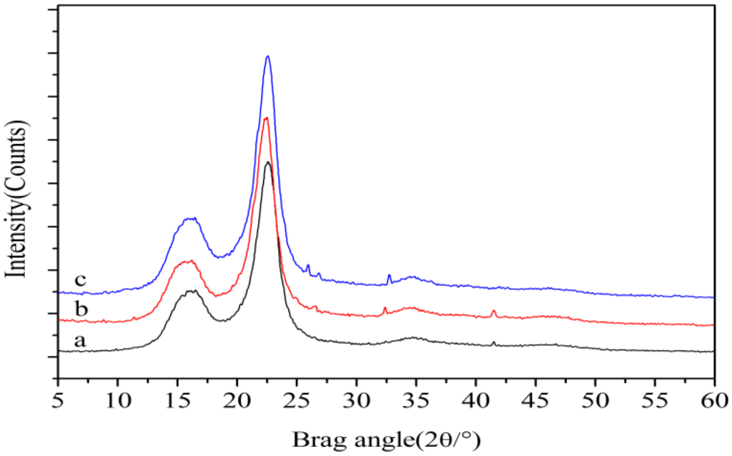


Fig. 3. XRD of samples (a = cellulose; b = hydrocellulose without $FeCl_3$ treatment; c = hydrocellulose with 0.3 M $FeCl_3$ treatment)

Regression Models of Response

The statistical treatment combinations of the test variables along with the measured response values, expressed as the crystallinity of hydrocellulose corresponding to each combination, are summarized in Table 2.

Table 3 shows the *F*-test and the corresponding *P*-value along with the parameter estimation. The lower the *P*-value, the higher the significance of the corresponding *P*-value coefficient (Majumder and Goval 2008). The model *F*-value of 43.40 and values of probability *(P)>F* (<0.0001) showed that the model terms were significant. The coefficient of variation (*CV*) indicated the degree of precision with which the treatments were compared. A relatively low value of *CV* (1.43%) indicated a better precision and reliability of the experiments (Hou and Chen 2008). The coefficient of determination (R^2) was calculated to be 0.98 for the crystallinity, indicating that the statistical model can explain 98% of the variability in the response. Normally, a regression model with an R^2 higher than 0.90 is considered to have a very high correlation (Duret *et al.* 2013). The parameter estimates and the corresponding *P*-values suggested that, among the independent variables, X_2, X_4 and X_1, X_3 have significant effects on the crystallinity of hydrocellulose.

Table 2. Central Composite Design Matrix and Results

Run	Code values				Crystallinity/%	
	X_1	X_2	X_3	X_4	Experiment values	Predicted values
1	-1	-1	1	1	60.65	60.03
2	-1	-1	-1	1	59.01	58.89
3	-1	-1	1	-1	49.93	50.79
4	-1	1	-1	-1	57.64	61.86
5	-1,546	0	0	0	59.78	58.55
6	-1	1	1	1	62.36	62.15
7	0	0	0	1.546	61.68	62.14
8	1	1	1	-1	60.99	60.90
9	-1	1	-1	1	61.79	61.01
10	0	0	0	0	60.86	59.25
11	0	0	0	0	57.94	59.25
12	0	0	0	0	58.76	59.25
13	1	1	1	1	62.42	63.37
14	1	-1	-1	-1	51.99	50.87
15	1	1	-1	1	62.02	62.23
16	-1	-1	-1	-1	49.52	49.66
17	0	0	0	-1.546	53.31	53.09
18	-1	1	1	-1	60.25	59.69
19	0	0	-1.546	0	58.50	58.37
20	0	-1.546	0	0	51.63	52.49
21	0	1.546	0	0	61.63	61.01
22	1.546	0	0	0	61.76	61.83
23	1	-1	1	-1	52.34	52.01
24	1	1	-1	-1	59.34	59.77
25	1	-1	1	1	61.47	61.25
26	1	-1	-1	1	60.13	60.11
27	0	0	1.546	0	60.35	60.13

Table 3. Analysis of Variance for the Quadratic Model

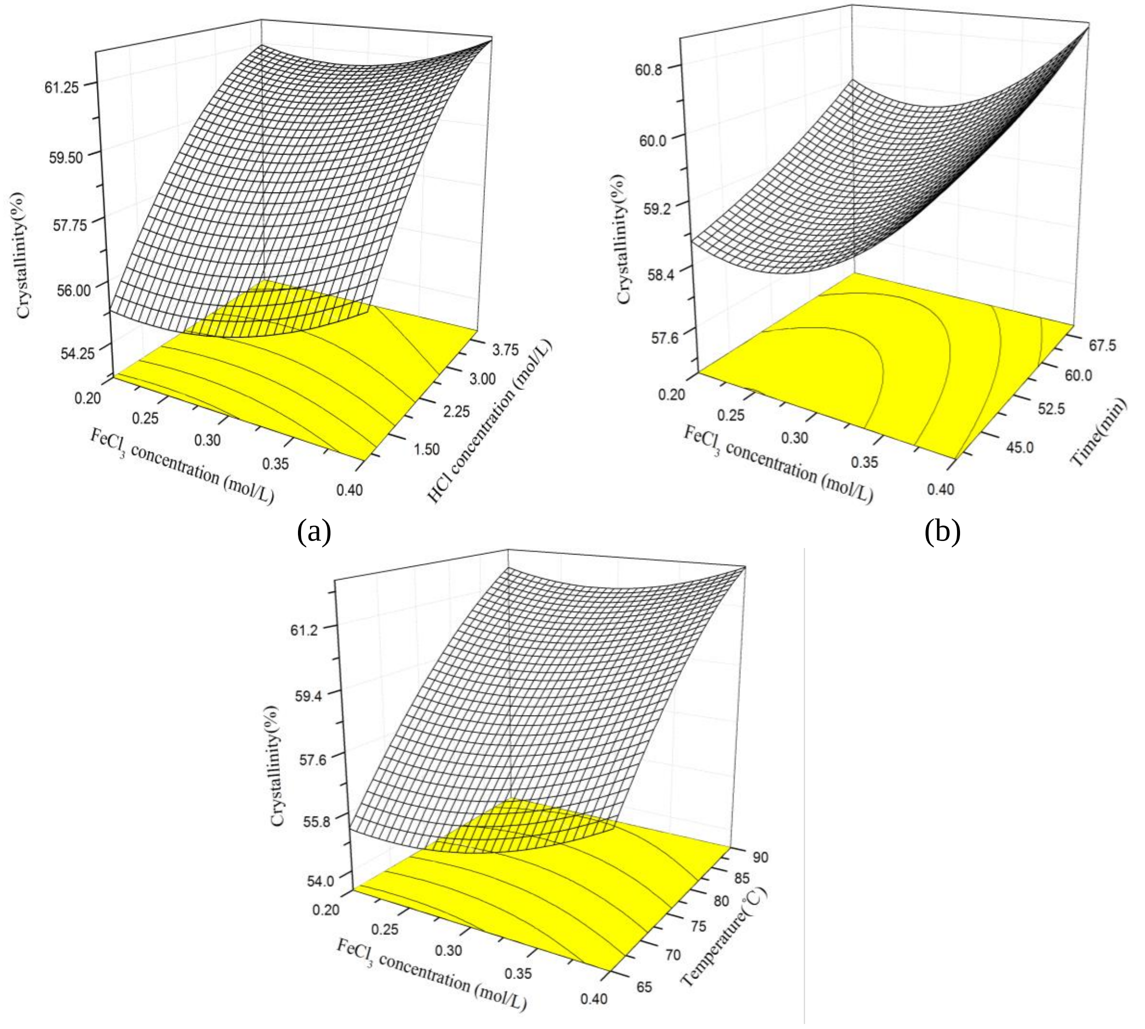
Source	Sum of Squares	df	Mean Square	F-Value	P -Value
Model	422.22	14	30.16	43.40	<0.0001
X_1	7.65	1	7.65	11.01	0.0061
X_2	157.62	1	157.62	226.81	<0.0001
X_3	6.73	1	6.73	9.69	0.0090
X_4	177.83	1	177.83	255.89	<0.0001
X_1X_2	1.05	1	1.05	1.50	0.2435
X_1X_3	0.14	1	0.14	0.20	0.6630
X_1X_4	1.62	1	1.62	2.23	0.1528
X_2X_3	0.14	1	0.14	0.20	0.6630
X_2X_4	45.93	1	45.93	66.1	<0.0001
X_3X_4	0.072	1	0.072	0.10	0.7538
X_1^2	5.35	1	5.35	7.70	0.0011
X_2^2	12.54	1	12.54	18.05	0.0018
X_3^2	0.17	1	0.17	0.24	0.6305
X_4^2	5.37	1	5.37	7.73	0.0166
Residual	8.34	12	0.69		
Lack of Fit	3.80	10	0.38	0.17	0.9803
Pure Error	4.54	2	2.27		
Cor Total	430.56	26			

*P-value less than 0.05 indicates model terms are significant. R^2=0.9806, The "Pred R-Squared" of 0.9268 is in reasonable agreement with the "Adj R-Squared" of 0.9580.

The quadratic terms of X_1, X_2, and X_4 and interactions between X_2 and X_4 also had significant effects on the crystallinity. A statistically significant model only with significant terms can be written as follows,

$$R=59.16+0.61X_1+2.75X_2+0.57X_3+2.93X_4-0.26X_1X_2-0.093X_1X_3-0.32X_1X_4 \\ +0.093X_2X_3-1.69X_2X_4-0.067X_3X_4+0.68X_{12}-1.05X_{22}+0.12X_{32}-0.69X_{42} \quad (4)$$

Figure 4 shows the response surface of the crystallinity. The crystallinity is represented as a function of $FeCl_3$ concentration and HCl concentration, reaction time, or temperature. As shown, the optimal crystallinity was mainly influenced by the HCl concentration and the temperature. The possible explanation is that acids can diffuse into the amorphous region and small part of surfaces of crystalline region. This indicated that the intermolecular hydrogen bonds and intramolecular glycosidic bonds of cellulose are easily fractured, which led to physical swelling along with the chemical degradation of cellulose.



(a) (b)

(c)

Fig. 4. Response surface plots and contour plots of the combined effects of $FeCl_3$ concentration and HCl concentration (a), reaction time (b), and temperature (c) on the crystallinity of hydrocellulose while other two factors were set at corresponding center points

Swelling of the cellulose increased the contact area between acids and cellulose, and hence improved the hydrolysis efficiency. The increase of the $FeCl_3$ concentration was beneficial to the improvement of the crystallinity when the HCl concentration was low (Fig. 4a). As can be seen from Fig. 4b, the influence of reaction time on the crystallinity was not appreciable. A significant increase in the crystallinity can be found when the temperature increased, and the contour plot showed that a high crystallinity of hydrocellulose was obtained at a higher temperature (Fig. 4c). This was in agreement with the predicted model. However, the results showed that the addition of $FeCl_3$ affected the selective acid hydrolysis of cellulose for MCC, and factors affecting the crystallinity of hydrocellulose were in the order of: reaction temperature > HCl concentration > $FeCl_3$ concentration > time.

Effect of Independent Variables on Crystallinity and Adequacy of the Models

The second-order polynomial regression equation obtained from the experimental data can be used to predict the crystallinity of hydrocellulose under various $FeCl_3$ concentrations, HCl concentrations, reaction temperatures, and times within the range of the experimental design. In order to confirm the validity of the statistical experimental strategies and gain a higher crystallinity of MCC by selective hydrolysis of cellulose, the optimum hydrolysis conditions were as follows: $FeCl_3$ concentration, 0.4 M; HCl concentration, 2.46 M; reaction temperature, 88.28 °C; and reaction time, 64.02 min; the crystallinity predictive value of hydrocellulose was 62.45%. The results of three parallel tests showed that the actual crystallinity of hydrocellulose was 63.59%. The percent error between the actual and predicted values for hydrolysis was observed to be 1.79%. The predicted values and actual experimental values were compared (Table 2), and the residual and percentage error calculated. Therefore, the empirical models developed were reasonably accurate, which verified that RSM analysis is indeed a useful technique to predict and optimize the selective acid hydrolysis of cellulose for microcrystalline cellulose preparation by $FeCl_3$.

CONCLUSIONS

1. $FeCl_3$ can be used as catalyst for selective hydrolysis of cellulose. Addition of $FeCl_3$ helps to improve the efficiency of acid hydrolysis and enhance the hydrolysis of amorphous regions compared with no catalyst.
2. X-ray diffraction results showed that the crystalline structure of cellulose was not changed by the acid hydrolysis treatment. Under the experimental conditions, the crystallinity of hydrocellulose after hydrolysis can be achieved at 63.59%, an increase of 13.61% compared to cellulose without the addition of $FeCl_3$.
3. The RSM was performed to optimize the acid hydrolysis selectivity of cellulose. The results showed that the concentration of $FeCl_3$ plays an auxiliary role on acid hydrolysis of cellulose. The regression equation was obtained by RSM, and theoretical crystallinity was obtained under following conditions: $FeCl_3$ concentration, 0.4 M; HCl concentration, 2.46 M; reaction temperature, 88.28 °C; and reaction time 64.02 min. The theoretical value of the crystallinity was 62.45%, while the actual value was 63.59%. Therefore, the RSM with CCD design is useful for

identifying and optimizing the important factors influencing acid hydrolysis selectivity of cellulose.

ACKNOWLEDGMENTS

This project was financially supported by the Specialized Research Fund for the Doctoral Program of Higher Education of China (grant NO.20126125130001), the State Key Lab of Pulp and Paper Engineering Open Fund (grant NO.201215), Shaanxi Province Natural Science Fund Project (grant NO.2013JM2007) and the Doctoral Scientific Research Fund by Shaanxi University of Science & Technology (grant NO.BJ13-02).

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Article submitted: December 10, 2013; Peer review completed: January 12, 2014; Revised version received: January 14, 2014; Accepted: January 18, 2014; Published: January 27, 2014.