

## EFFICIENT PROCESS OF DEASHING STRAW CELLULOSE

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Crop straw cellulose always contains a high percentage of ash, which seriously restricts its high-value-added applications. In this study, two dilute mixed aqueous solutions (NaF-HCl and HF-HCl) have been used to treat raw rice straw cellulose and the optimized conditions have been determined as: temperature of 60 °C, treatment time of 2 h with 34.0 wt% NaF in 2.0 wt% HCl aqueous solution, and temperature of 60 °C, treatment time of 6 h with 1.5 wt% HF in 2.0 wt% HCl aqueous solution. Under the optimal conditions, 96.15% and 99.93% ash could be removed, respectively. It was demonstrated that such deashing processes had no obvious impact on the chemical properties of cellulose, while the crystallinity was relatively improved. The results of ICP analysis proved that HCl, NaF and HF had different effects on ash elements. After deashing, the solution can be recycled to obtain H<sub>2</sub>SiF<sub>6</sub>, which is a useful preservative and a raw material for production of fluosilicate and silicon tetrafluoride.

**Keywords:** deashing, rice straw cellulose, NaF-HCl aqueous solution, HF-HCl aqueous solution, recyclable, H<sub>2</sub>SiF<sub>6</sub>

## INTRODUCTION

Crop straw, one of the most important types of plant biomass, is mainly composed of cellulose, hemicellulose and lignin, of which, cellulose takes the largest proportion of 30-50%.<sup>1,2</sup> Straw cellulose has been successfully isolated from agricultural residues in many eco-friendly ways,<sup>3,4</sup> which is a good alternative to cotton, hemp and wood, to be utilized in textiles, paper making, high-performance composites and other light industry fields. Thus, it is important to improve the application technology of straw cellulose in relevant fields.<sup>5</sup> However, such cellulose usually has high ash content, which limits its high-value utilization, *e.g.* ash content must be less than 0.13 wt%, according to the standard of Chinese viscose fiber pulp (FZ/T 50010.5). Inorganic impurities, such as silicon, calcium and magnesium, from the ash will react with the carboxyl groups of cellulose to generate insoluble salts, which are difficult to remove.<sup>6</sup> Besides, inorganic impurities also accelerate the aging of cellulose and impair the performance and quality of cellulosic fiber. Therefore, an effective deashing process is essential for straw isolated cellulose intended to be used for spinning or other high-value

applications.<sup>7</sup> Meanwhile, there are few reports on deashing of cellulose. Moreover, chemical processes are predominant in this area. According to some studies,<sup>8,9</sup> cooking cellulose with an alkali solution could improve the dissolution of the ash, and result in removing more than 94% ash under optimized conditions, where the alkali concentration was a most important factor.<sup>10</sup> However, the caustic alkali solution destroyed the fibrous structure. Li<sup>11</sup> applied Na<sub>3</sub>PO<sub>4</sub> and sodium hexametaphosphate as deashing reagents in an alkali system. It was supposed that the deashing agents acted directly on cellulosic materials to remove metallic elements efficiently. Also, dilute HCl and HF aqueous solutions were applied to remove ash from sugarcane bagasse for improving the further pyrolysis.<sup>12</sup> Herein, dilute NaF-HCl and HF-HCl aqueous solutions were used for deashing efficiently rice straw cellulose under mild conditions. The structure and properties of the deashed cellulose was not significantly affected and the deashing solutions could be recycled to obtain H<sub>2</sub>SiF<sub>6</sub>.

## EXPERIMENTAL

### Materials

The rice straw cellulose was supplied by Sichuan Baikaiwei Technology Co., Ltd., with 3.8000 wt% ash content, 75.2200 wt%  $\alpha$ -cellulose, 4.7000 wt% pentosan and DP of 403. The isolation procedure had been reported earlier by our research group.<sup>13</sup> Sodium fluoride (NaF) was purchased from Aladdin Chemistry Company, China. Hydrochloric acid (HCl) and hydrofluoric acid (HF) were purchased from Chengdu Kelong Chemical Industry. All reagents were of analytical grade and were used directly.

### Deashing processes

The straw cellulose was dried in an oven at 90 °C overnight and then crushed into powder in a shredder (FW400A, Beijing Zhongxing Industry Co., Ltd.) before use. With a solid to liquid ratio of 1:30 (g/ml), the crushed cellulose was cooked with NaF-2.0 wt% HCl or HF-2.0 wt% HCl aqueous solution under the given conditions.

### Characterization and analysis

Fourier transform infrared (FT-IR) analysis was performed on a Nicolet 5700 spectrometer (Nicolet Instruments, USA). The spectra were recorded in the wavenumber range of 400-4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The crystalline structure of the samples was examined by a wide angle X-ray diffractometer (XRD) (Philip X'Pert PRD, Japan) at room temperature. The diffraction patterns were recorded over a  $2\theta$  range of 5-80°. The operating voltage and current were 40 kV and 40 mA, respectively. The radiation was Ni-filtered Cu-K $\alpha$  radiation of 1.54056 Å wavelength. The morphology of the samples was characterized by a scanning electron microscope (SEM) (QUANPA200, Netherlands) in high vacuum mode with an accelerating voltage of 5 kV. The ash content of the cellulose was detected according to the modified Chinese standard GB/T 742-2008 method. The procedure mainly included completely drying a 0.1 g cellulose sample under 90 °C for 12 h before weighing, calcining it at 700 °C for 2 h, then cooling to room temperature in a desiccator and weighing. The inorganic elements of cellulose, before and after deashing, were analyzed by inductive coupling plasma emission spectroscopy (ICP).

## RESULTS AND DISCUSSION

### Deashing straw cellulose with NaF-HCl and HF-HCl dilute aqueous solutions

In the investigation that involved the NaF-HCl aqueous solution for deashing straw cellulose, the effects of NaF concentration, cooking time and temperature on deashing efficiency were studied through orthogonal experiments ( $L_{16}(4)^4$ ). The arrangement and results are summarized in Table 1. The inspected factors affected the deashing

efficiency in the following order: NaF concentration ( $R = 29.168$ ), cooking time ( $R = 14.422$ ) and then temperature ( $R = 11.855$ ). The efficiency of deashing was significantly improved when the concentration of NaF was increased from 10.0 to 34.0 wt%. The deashing efficiency was up to 96.15%, when the concentration of NaF was 34.0 wt%, and the ash content was decreased to 0.1380%, which completely met the requirement of cellulose wet spinning, according to the Chinese Ministry of Textiles Standard FJ517-82 ( $<0.2\%$ ). It was concluded from Table 1 that the optimal deashing conditions for the NaF-HCl aqueous solution treatment were: 60 °C, 2 h cooking time and 34.0 wt% NaF concentration. According to the element analysis by the ICP method, there were 39.3400 wt% silicon, 8.6000 wt% calcium, 0.4100 wt% magnesium and 0.8100 wt% iron elements in the raw straw cellulose. The content of silicon accounted for 80-90 wt% of the total ash content. Therefore, the removal of silicon was the most significant in the deashing process.

Thereafter, the HF-HCl aqueous solution was also investigated with a group of  $L_9(3)^3$  orthogonal experiments. The HF concentration, cooking time and temperature were examined. The experiment conditions and results were included in Table 2. It was shown that the HF concentration was also the dominating factor for the deashing efficiency. With the increase of HF concentration from 0.5 to 1.5 wt%, the deashing efficiency was improved from 90.77 to 95.13%. However, the optimal conditions obtained from the orthogonal analyses were not found among the experimental conditions listed in Table 2. With the increase of HF concentration and the extension of cooking time, the deashing efficiency improved continuously. Therefore, a supplementary set of experiments was conducted, as listed in Table 3.

Considering the deashing efficiency and comprehensive benefits, the raw straw cellulose was cooked in HCl aqueous solution at 60 °C for 6 h with 1.5 wt% HF. As shown in Table 3, more than 99.9% ash was removed under the optimal conditions.

### Characterization of straw cellulose before and after deashing

Figure 1 shows the SEM images of the cellulose samples before and after deashing with NaF-HCl and HF-HCl aqueous solutions, respectively. After the treatment with the NaF-HCl or HF-HCl aqueous solution, the

morphology of cellulose did not change obviously. Compared with the raw cellulosic fiber (Fig. 1a), the morphology of the deashed cellulosic fibers (Fig. 1 b, c) showed no obvious difference, except that the diameter decreased slightly.

Natural straw cellulose is a partially crystalline polymer, and its mechanical properties are closely

dependent on its crystallinity and molecular orientation. Figure 2 illustrates the XRD patterns of the cellulose samples before and after the deashing treatment. All the samples show three strong peaks at 15.3°, 22.6° and 34.5° assigned to the cellulose-I crystal.<sup>14</sup> The peak located at 22.6° is characteristic of the (200) plane, and the peak at 34.5° corresponds to the (400) plane.

Table 1  
Orthogonal experimental conditions for NaF-HCl deashing process and the results<sup>a</sup>

Number	NaF concentration A (wt%)	Cooking time B (h)	Cooking temperature C (°C)	Deashing efficiency (%) <sup>b</sup>
1	10.0	0.5	15	43.59
2	10.0	1.0	25	51.28
3	10.0	1.5	60	61.54
4	10.0	2.0	80	64.10
5	17.0	0.5	60	64.10
6	17.0	1.0	80	61.54
7	17.0	1.5	15	61.54
8	17.0	2.0	25	94.87
9	27.0	0.5	80	76.92
10	27.0	1.0	60	82.05
11	27.0	1.5	25	69.23
12	27.0	2.0	15	66.67
13	34.0	0.5	25	84.62
14	34.0	1.0	15	84.62
15	34.0	1.5	80	71.79
16	34.0	2.0	60	96.15
K <sub>1</sub>	55.127	67.308	64.105	
K <sub>2</sub>	70.512	69.873	75.000	
K <sub>3</sub>	73.718	66.025	75.960	
K <sub>4</sub>	84.295	80.447	68.588	
R	29.168	14.422	11.855	

<sup>a</sup> Before deashing, straw cellulose contained 3.8 wt% ash

<sup>b</sup> Deashing efficiency was calculated by dividing the ash content value after deashing by that of the raw straw cellulose (3.8 wt%)

Table 2  
Orthogonal experimental conditions for HF-HCl deashing process and the results

Number	HF concentration A (wt%)	Cooking temperature B (°C)	Cooking time C (h)	Deashing efficiency (%)
1	0.5	25	0.5	90.77
2	0.5	60	1.0	91.03
3	0.5	80	2.0	92.31
4	1.0	25	1.0	91.54
5	1.0	60	2.0	95.38
6	1.0	80	1.0	93.08
7	1.5	25	2.0	92.56
8	1.5	60	1.0	95.13
9	1.5	80	2.0	95.13
K <sub>1</sub>	91.370	91.623	92.993	
K <sub>2</sub>	93.590	94.103	92.567	
K <sub>3</sub>	94.273	93.507	93.673	
R	2.903	2.480	1.106	

Table 3  
Further experimental conditions for HF-HCl deashing process and the results

Number	HF concentration A (wt%)	Cooking temperature B (°C)	Cooking time C (h)	Deashing efficiency (%)
1	1.5	60	2	96.15
2	1.0	60	2	95.38
3	2.0	60	2	99.76
4	1.5	60	3	97.18
5	1.5	60	4	96.15
6	1.5	60	5	98.21
7	1.5	60	6	99.93



Figure 1: SEM photographs of straw cellulose before deashing (a), and after deashing with NaF-HCl aqueous solution (b) and HF-HCl aqueous solution (c)

It is obvious that no crystal transformation occurred during the deashing process.

As shown in Figure 2, the intensity of the diffractions associated with the characteristic peaks of cellulose became stronger after the deashing treatment. Crystallinity was calculated from the diffracted intensity data, using the empirical method proposed for native cellulose,<sup>15,16,17</sup> as shown below:

$$Cr.I. = \frac{I_{200} - I_{am}}{I_{200}} \times 100$$

where *Cr.I.* is the degree of crystallinity,  $I_{200}$  is the maximum intensity of the (200) lattice diffraction and  $I_{am}$  is the intensity diffraction at 2θ degrees between 18 and 20. Accordingly, the values of *Cr.I.* were calculated to be 56.840, 67.080 and 65.740% for the raw cellulose and the deashed cellulose with the NaF-HCl aqueous solution and the HF-HCl aqueous solution, respectively. It was obvious that the crystallinity of the straw cellulose lightly increased after the deashing treatment.

The FT-IR spectra of the straw cellulose before and after being treated with the NaF-HCl aqueous solution or the HF-HCl aqueous solution are shown in Figure 3. The three spectra show apparently the same absorptions, which proves that no obvious changes happened in the chemical structure during the deashing process. This is

consistent with the results of XRD analysis.

Hydrogen bonds have a considerable effect on the configuration of cellulose. Due to the different intra- and inter-molecular hydrogen bonds, the FT-IR spectra of cellulose are different.<sup>18,19</sup> The values of  $H_{1429}/H_{897}$  represent the degree of crystallinity.<sup>20-22</sup> Based on it, the degrees of crystallinity were calculated to be 0.358, 0.550 and 0.368 for the raw cellulose and the deashed cellulose with the NaF-HCl aqueous solution and the HF-HCl aqueous solution, respectively, which was in accordance with the results calculated by the XRD method.

The DP, pentosan content, α-cellulose content and ash content of the straw cellulose were analyzed before and after the deashing treatment according to the standard methods of FZ/T50010.3-2011, GB2677.10-1981 and GB/T745-2003, and the results were summarized in Table 4. Compared with the raw straw cellulose (DP = 403), there was an obvious decrease for the cellulose deashed with the HF-HCl aqueous solution (DP = 342). The pentosan content remained the same (4.7000 wt%), but the α-cellulose content decreased from 75.2200 to 68.8900 wt%. It was concluded that the HF-HCl aqueous solution was efficient in deashing straw cellulose, except that the cellulose long molecular

chains were partially broken. Besides, the pentosan content was decreased from 4.7000 to 2.8000 wt% after deashing with the NaF-HCl aqueous solution. So, the increase of the DP value

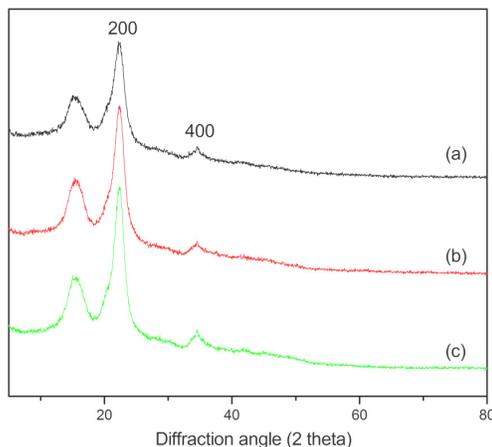


Figure 2: X-ray diffraction patterns of the straw cellulose before deashing (a), the NaF-HCl aqueous solution treated straw cellulose (b) and the HF-HCl aqueous solution treated straw cellulose (c)

from 403 to 546 after the deashing treatment was attributed to the decrease in the ash and pentosan contents.

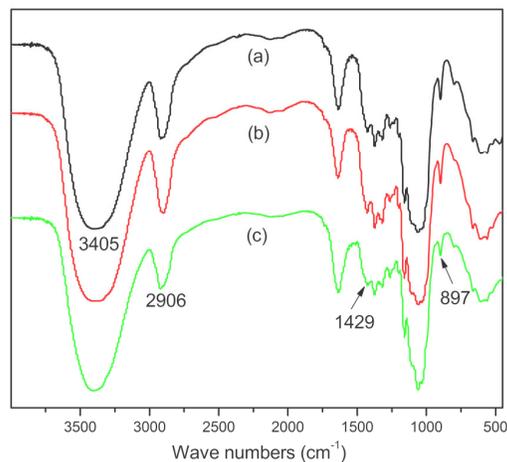


Figure 3: FT-IR spectra of the straw cellulose before deashing (a), the NaF-HCl aqueous solution treated cellulose (b) and the HF-HCl aqueous solution treated cellulose (c)

Table 4  
Analysis of straw cellulose before and after deashing

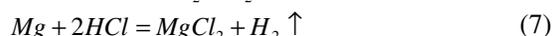
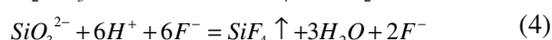
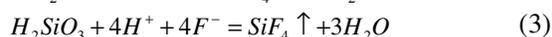
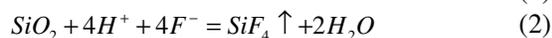
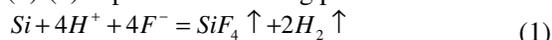
Sample	DP	Pentosan (wt%)	$\alpha$ -cellulose (wt%)	Ash content (wt%)
Raw sample	403	4.7000	75.2200	3.8000
Deashed sample 1 <sup>a</sup>	342	4.7000	68.8900	0.0027
Deashed sample 2 <sup>b</sup>	546	2.8000	73.1200	0.0032

<sup>a</sup> Deashed sample 1 was treated with 1.5 wt% HF-2.0 wt% HCl aqueous solution at 60 °C for 2 h;

<sup>b</sup> Deashed sample 2 was treated with 34.0 wt% NaF-2.0 wt% HCl aqueous solution at 60 °C for 6 h

### Discussion of the deashing mechanism

To validate the roles of HCl, HF and NaF in the deashing process, further experiments were conducted as shown in Table 5. It could be seen that only HF or NaF aqueous solutions could not remove the ash from the straw cellulose efficiently. When the HF-HCl aqueous solution or the NaF-HCl aqueous solution was applied, the ash content was reduced to 0.009 and 0.011 wt%, respectively. It was manifested that F<sup>-</sup> from NaF and HF reacted with silicon in the presence of H<sup>+</sup> to remove the ash sufficiently. Chemical reactions (1)-(4) express the deashing process:



During the process, metallic elements, such as calcium, magnesium and iron, were mainly captured by HCl, as shown in reactions (5), (6) and (7). HCl also played an auxiliary role in the desilicisation conducted by NaF or HF.

The metallic elements existing in the straw cellulose before and after being deashed were detected by ICP, and the results are listed in Table 6a. At the same time, the recovered deashing solutions were analyzed, as shown in Table 6b. It should be mentioned that the metal element contents listed in Table 6a were calculated based on the metal-oxide content. This explains why the total content was not 100%. After deashing with the HCl aqueous solution, there was a significant

decrease in the contents of calcium, magnesium and iron elements.

That is to say, HCl mainly took effect on capturing them in this process. As seen from Table 6b, it could be further concluded that F<sup>-</sup>

together with H<sup>+</sup> performed quite well in capturing Si (6780 mg/L), Mg (142 mg/L) and Fe (81 mg/L). As to the Ca element, Cl<sup>-</sup> together with H<sup>+</sup> gave the highest efficiency (692 mg/L).

Table 5  
Experimental conditions and the results for validating the deashing mechanism\*

Sample	HF concentration (wt%)	NaF concentration (wt%)	HCl concentration (wt%)	Ash content (wt%)
1	1.5	—	—	1.0900
2	—	34.0	—	2.2400
3	1.5	—	2.0	0.0090
4	—	34.0	2.0	0.0110
5	—	—	2.0	2.9300

\* The deashing experiments were all carried out at 60 °C for 6 h, and the raw straw cellulose was determined to contain 3.8000 wt% ash

Table 6a  
Inorganic elements analysis of the straw cellulose before and after deashing

Deashing aqueous solution	Na (%)	Si (%)	Ca (%)	Mg (%)	Fe (%)
None	—	39.34	8.60	0.81	0.43
HCl	—	46.29	0.40	0.07	0.07
NaF	6.56	33.59	9.43	0.58	0.85
HF	—	1.16	45.40	0.52	0.54
HF-HCl	—	20.88	7.42	0.93	4.45
NaF-HCl	13.70	22.59	15.69	1.26	0.64

Table 6b  
Inorganic elements analysis of the recovered deashing solutions

Recovered deashing aqueous solution	Na (mg/L)	Si (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)
Distilled water	—	—	—	—	≤0.0004
HF	—	6780.0	639.0	142.0	81.0
NaF	18.5	503.0	8.2	2.2	19.6
HCl	—	229.0	692.0	35.1	67.7

### Recovery of the deashing solution

As known, F<sup>-</sup> can react with silicon to generate H<sub>2</sub>SiF<sub>6</sub>, which is a very useful preservative for wood, as well as a raw material for the production of fluosilicate (sodium, potassium, ammonium, magnesium, copper, barium, lead *etc.*) and silicon tetrafluoride.<sup>23,24</sup> Before recovering the deashing solution, the concentration of F<sup>-</sup> was detected in accordance with the standard method of HGT2832-2008. However, no free F<sup>-</sup> was detected, which indicated that F<sup>-</sup> might be completely transformed into H<sub>2</sub>SiF<sub>6</sub>. In this work, 2 ml HF was used to treat 3 g straw cellulose, and the recovered solution was carefully concentrated to get 2.600 wt% H<sub>2</sub>SiF<sub>6</sub> aqueous solution.

### CONCLUSION

Two dilute aqueous solutions (NaF-HCl and HF-HCl) have been applied to deash straw cellulose to meet the requirement for high-value applications. After the treatment, the ash content decreased from 3.8000 to 0.0110 and 0.0009 wt%, respectively, under the optimized conditions (60 °C, 6 h and 34.0 wt% NaF for the NaF-HCl treatment, and 60 °C, 6 h and 1.5 wt% HF for the HF-HCl treatment). During the deashing process, F<sup>-</sup> together with H<sup>+</sup> performed quite well in capturing Si, Mg and Fe, while Cl<sup>-</sup> together with H<sup>+</sup> gave the highest efficiency in eliminating Ca. The NaF-HCl aqueous solution can not only effectively reduce the ash content, but also

significantly remove the residual pentosan to upgrade straw cellulose. Finally, the deashing solution has been recovered as  $\text{H}_2\text{SiF}_6$ . The process described in this work can be also applied in the purification of the cellulose of other plants in order to broaden its applications.

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