Optimization of Removal of Lignin from Corn Stover by Urea

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Abstract. Corn stover in rich source was taken as the research object. The pre-treatment process of corn stover by urea was proposed. The effects of urea amount, temperature, time and the ratio of solid-liquid on the degradation of lignin were investigated. The results showed that urea had a definite degradation effect on lignin and hemicellulose in corn stover. The optimum experimental conditions were as follows: 8g corn stover, 0.8g urea and 80ml water were added in triangle bottle. The degradation was carried out for 4 h shocked with 170 r/min speed in a thermostatic water bath oscillator at 60°C temperature. The degradation rate of lignin was about 40%. The regent of urea was environment friendly and the method was prospect for practical application.

1. Introduction
The consumption of non-renewable energy such as oil has led to energy crisis and environmental pollution. The research of biomass energy was one of the focus points of renewable resources [1]. A great concern was to prepare clean fuels and bio-based chemicals from lignocellulosic biomass to supply or replace petroleum chemicals [2, 3].

Straw, as a biomass resource with extensive resources, was composed of about 70% carbohydrates, namely cellulose and hemicellulose, which can be converted into fermentable sugars and further used to produce ethanol, methane, single-cell protein and microbial metabolites [4, 5]. The pre-treatment of biomass cellulose was the key step of converting lignocellulose into fermentable sugar. The complex structure of lignocellulose makes it difficult for cellulase directly contacting with cellulose, so resulting in low efficiency of biodegradation for cellulose [6, 7]. The aim of pre-treatment of straw was to remove some lignin and degrade amount of hemicellulose, and so destroy the wrapping of lignin and hemicellulose on cellulose. Through the pre-treatment process, the cellulose was de-crystallization and looseness, which promote the contact between enzyme or yeast with substrate and improve the yield of fermentable sugar [8, 9]. The inorganic acid and base method was the traditional separation method for lignin. However, the inorganic alkali method requires a large amount of water to wash out salt and detoxify the substrate after pre-treatment, and so the waste water was not easy to recycle and produce a great impact on the soil environment [10]. In addition, the inorganic acid method will cause corrosion to the equipment, which will increase the operation and maintenance cost on the equipment [11, 12]. In recent years, removal of lignin by organic solvent method has become a hot research point, in which, the most low pollution solvents could be recycled [13, 14]. Further, by
using these methods, not only cellulose can be exposed, but also better quality lignin can be recovered [15].

In this paper, corn stover, which was the straw with the highest crop yield in China [16], was selected as lignocellulosic biomass material, and the optimized operating conditions for removal of lignin by environmentally friendly urea was discussed.

2. Experimental

2.1. Materials
The corn stover was come from the Molda Dawa Daur Autonomous Banner, Hulun Beir, Inner Mongolia. Corn stover was pretreated following steps of washing, drying, pulverizing, sieving with 60 mesh sieves, sealing and storing. Urea was acquired from Shentai Chemical Reagent Ltd. (Tianjin, China).

2.2. Analysis of components in in corn stover
Determination of the main components such as lignin, cellulose and hemicellulose in corn stover was follow procedures as below, which reference to Van Soest’s method [17]

2.3. Removal of lignin from corn stover
Weighed 8g of corn stover and put in a 250ml triangle bottle, in which, added a certain amount of urea and a definite proportion of water, and sealed it with polyethylene film. The triangle bottle was shocked at different temperatures for a certain time with 170 r/min speed in a thermostatic water bath oscillator. Then, the content was pumped with 250 ml G3 glass core funnel and the filter residue was washed with distilled water until the filtrate was neutral. The filter residue was dried at 105°C for about 6 h until weight constant. The got sample was sealed in a desiccator with a sealed bag for detecting use.

3. Results and discussion

3.1. Content of Various Components of Corn stover
The main components in corn stover were shown in Table 1.

| Component       | Quality Score (%) | Component       | Quality Score (%) |
|-----------------|-------------------|-----------------|-------------------|
| Hemicellulose   | 33.33             | Lignin          | 11.14             |
| Cellulose       | 40.34             | Ash             | 5.3               |

3.2. The Effect of Various Factors on the Yield of Lignin
The main factors, such as mass concentration of urea, temperature and time, influencing on lignin removal efficiency were discussed.
3.2.1. **Effect of Urea amount on Lignin Removal.** Amount of urea to corn stover was the important factor to impact on the removal of lignin. The amount of fixed corn stover was 8g and different proportions of urea were added in 250ml triangle bottle respectively, then dissolved with 80ml distilled water, and then shocked at a temperature of 30°C for 4h with 170 r/min speed in a thermostatic water bath oscillator. The results were shown in Figure 1.

![Figure 1. Effect of the amount of urea on components](image)

As could be seen from Table 1, with changing of the urea proportion, the content of lignin, cellulose and hemicellulose in corn stover all changed. The content of lignin and hemicellulose decreased rapidly as the mass proportion of urea continuously increased from 6% to 9%, on the contrary, cellulose increased quickly. When the proportion of urea continuously increased, the content changing of lignin, hemicellulose and cellulose were not obvious and the trend lines were nearly to be flat. This phenomenon indicated that hemicellulose was degraded by urea and peeling reaction occurs at beginning, and so resulting the content of hemicellulose initially decreased rapidly. For the alkali solubility characteristic of lignin, the increased the OH- concentration by increasing urea was benefit to lignin dissolution. With more lignin was exposed, the lignin dissolution rate increased and the contact area with lignin increased. After urea mass concentration reaches 9%, lignin dissolution reached equilibrium. Therefore, it was preliminaries determined that the mass concentration of urea to corn stover was 10%, and the lignin removal rate was about 30%.

3.2.2. **Effect of Reaction Temperature on Lignin Removal.** Weigh 8 g of corn stover in 250ml triangle bottles respectively, add 0.8g urea and 80ml of distilled water, then shocked at different temperatures for 4h with 170 r/min speed in a thermostatic water bath oscillator. The results were shown in Figure 2.

It could be seen from Figure 2, in treated corn stover, the content of lignin and hemicellulose decreased and the content of cellulose increased with the temperature raised. Lignin did not substantially degraded at 20°C,which could be explained by that this condition did not suitable for lignin degraded owing to urea was not hydrolyzed to produce OH- and the solution was almost neutral. The content of lignin decreased rapidly as the temperature raise from 20°C to 30°C for urea hydrolyzed thoroughly at higher temperature and the higher solubility of lignin resulted. The contents of lignin, hemicellulose and cellulose were not changed obviously. When the temperature reaches to 60°C, dissolves of lignin reached equilibrium, so the content of lignin no longer changed. And the contents of hemicellulose and cellulose tended to be stable. Therefore, the temperature at which lignin
was removed from corn stover by urea was determined to be 60°C, and the lignin removal rate was about 40%.

3.2.3. Effect of reaction time on lignin removal. The pretreated time was most important factor for lignin removal from corn stover considering the cycle and the cost. Weigh 8 g of corn stover in 250 ml triangle bottles, 0.8g urea and 80ml of distilled water were added respectively, then shocked for certain time with 170 r/min speed in 60 ℃ water bath thermostat. The results were shown in Figure 3.

As could be seen in Figure 3, the content of cellulose, hemicellulose and lignin in corn stover all changed with reaction time prolonged. At first two hours, the concentration of urea was higher and so
made hemicellulose and lignin content decreased rapidly, and cellulose relatively increased. When the reaction time prolong to 4 hours, the content of lignin reached the lowest point. When further prolong the reaction time, hemicellulose and lignin no more decreased and reached equilibrium. For the presence of a base, cellulose began undergoing alkaline hydrolysis. So, after 4h, the line of hemicellulose and lignin began to rise and the line of cellulose began to decrease. Therefore, it was determined that the time for retreat lignin by urea was 4 h, and the lignin removal rate was about 40%.

3.2.4. Effect of solid-liquid ratio on removal of lignin. The solid-liquid ratio was defined as the proportion of the weight of corn stover to the volume of water. Weigh 8 g of corn stover in 250 ml triangle bottles, 0.8 g urea was added, different volume distilled water was used to dissolve respectively, then shocked 4 h with 170 r/min speed in 60 °C water bath thermostat respectively. The results were shown in Figure 4.

![Figure 4. Effect of solid-liquid ratio on components.](image)

The changed solid-liquid ratio has a certain impact on the removal of lignin. As shown in Figure 4, when the solid-liquid ratio was 1:6, the concentration of OH- was higher, and the hemicellulose degradation rate was higher than the lignin degradation rate due to preferential contact. When the solid-liquid ratio increased from 1:6 to 1:8, the hemicellulose decreased faster than that of lignin. As the solid-liquid ratio increased further, the OH-concentration in the solution reduced, and the hemicellulose degradation rate was lower than that of lignin. When the ratio of solid to liquid was 1:10, the lignin content was the lowest and the cellulose content was the highest. When the solid-liquid ratio was 1:15, owing to the OH-concentration was too low and the reaction was slow in a unit time, the residual content of lignin was higher. Therefore, it was determined that the solid-liquid ratio was 1:10, and the lignin removal rate was about 40%.

4. Conclusions
Urea was used as a reagent for removal of lignin from corn stover, and the components, such as cellulose, hemicellulose and lignin, in corn stover were analysed before and after treatment. The lignin dissolution rate was about 40% at the following optimum conditions: weigh 8 g of corn stover, 0.8 g urea and 80 ml of distilled water, and then shocked with 170 r/min speed 4 h in 60 °C water bath thermostat. The experimental results showed that the rate of removal lignin by urea method was higher than that by the methods of H2SO4, CaO and H2O2 [18]. For the regent of urea was environment friendly, this method has a very good application prospect.
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