Kinetic Analysis of Pulping of Rice Straw with \( p \)-Toluene Sulfonic Acid

Qinghui Duan, Xudong Shuai, Dongmei Yang,* Xinkai Zhou, and Ting Gao

ABSTRACT: The kinetics of pulping of rice straw was studied with \( p \)-toluenesulfonic acid (\( p \)-TsOH). Pulping with 50% \( p \)-TsOH aqueous solution was performed at 70–100 °C for 0–360 min. The results showed that the delignification reaction could be divided into two phases: the bulk delignification phase and the supplementary delignification phase. Lignin dissolution was the main process in the bulk delignification stage, accompanied by the degradation of a small amount of carbohydrates. In the supplementary delignification stage, the delignification rate was low and carbohydrate degradation was severe. The degradation of carbohydrates is mainly based on the dissolution of hemicellulose. A combined delignification factor (CDF) and a combined hydrolysis factor (CHF) were used to compare severity-based kinetic analyses. The results showed that the degradation for lignin and hemicellulose can be well-fitted using CDF and CHF models. The fitted results show that the activation energy of the hemicellulose loss reaction and delignification reaction was 68.21 and 46.05 kJ/mol, respectively. Therefore, the use of \( p \)-TsOH for pulping is a technology with very broad application prospects.

1. INTRODUCTION

Sulfite pulping (KP) and sulfitic pulping are commonly used in traditional chemical pulping, in which KP occupies the dominant position in alkali pulping. However, there are shortcomings in KP, such as a relatively high pulping temperature is required to achieve a sufficient rate and extent of delignification and large investment scale. Compared with traditional pulping, organic solvent pulping has the advantages of high yield, high strength, low pollution, and good development prospects, including phenols, methanol, ethanol, butanol, ketones, and organic acids. At present, organic acid pulping and organic alcohol pulping are mainly studied. Organic solvents used for rice straw pulping include butanol, ethanol, soda-ethanol-water, and dimethylformamide; ethanol-water; a mixture of diethylene glycol and ethylene glycol and a mixture of diethylene glycol, ethylene glycol, and 2% NaOH; dimethylformamide; formic acid; and acetic acid. However, organic solvent pulping has not been commercialized because of difficulties in chemical recovery.

In order to control the cooking process, the mechanism and kinetics of delignification with different organic solvents have been studied by various researchers. Singh et al. studied the delignification process of wheat straw buffered by sodium hydroxide sulfate ions and found that the delignification kinetics was a second-order reaction. Park et al. systematically studied the mechanism and kinetics of delignification and the silicon removal reaction from rice straw and suggested that both were first-order reactions. Sabatier et al. studied the delignification of bagasse with three different degrees of air-drying by caustic soda cooking. The results showed that the delignification reaction of bagasse was divided into two stages: bulk delignification and residual delignification, in which the removal of hemicellulose promoted the delignification reaction, but the delignification reaction was more difficult with an increase in the degree of bagasse drying. Shatalov and Pereira studied the degradation kinetics of giant reed (\textit{Arundo donax}) ethanol-alkali delignification polysaccharide. The degradation reaction of cellulose and xyl-o-oligosaccharide proceeded slowly at a rate lower than 2 to 3 orders of magnitude with the second part of the pulping process.

Pulping with \( p \)-toluene sulfonic acid (\( p \)-TsOH) is advantageous based on the research by Chen et al., who used \( p \)-TsOH to rapidly dissolve lignin at low temperature with little damage to hexose. Zhu et al. studied the reaction severity of \( p \)-TsOH for poplar-based kinetic analysis and proved that it
was highly selective in preserving cellulose and the dissolution of lignin and hemicelluloses. Therefore, \( p \)-TsOH can be used in pulping not only with low energy consumption but also with a simple low-temperature cooking process. Because \( p \)-TsOH removes a substantial amount of hemicelluloses, it therefore has a low pulp yield,\(^{28}\) but it is beneficial for producing dissolved pulp and sugars.\(^ {27}\) One benefit is the preservation of the lignin and cellulose structure.\(^ {28}\) Besides, \( p \)-TsOH does not remove silica that is rich in rice straw, which not only is quite important to yield but also improves the downstream process runnability by eliminating the silica scaling issue, a huge problem in alkaline pulping of straw.\(^ {29}\) Additionally, because \( p \)-TsOH is a solid at room temperature, it can be recovered from waste liquid using simple separation methods such as crystallization. In conclusion, \( p \)-TsOH pulping can provide a new alternative for efficient and clean pulping technology.

The goal of this work is to establish the delignification kinetics of the main phenomena involved in the \( p \)-TsOH pulping of rice straw under atmospheric pressure. Temperature and reaction time were considered as operational variables. From the experimental data, kinetic models providing a quantitative interpretation of the experimental results were developed. This understanding provides a basis for optimal control of the pulping process.

2. RESULTS AND DISCUSSION

2.1. Selectivity of Lignin and Carbohydrate. Figure 1 shows the residual lignin content of rice straw \( p \)-TsOH pulping at different pulping temperatures. As shown in Figure 1, with the prolongation of cooking time, there are two types of straight lines of the slope for the residual lignin content, which are the two phases of delignification: the straight line with a higher slope indicates the bulk delignification phase, while the straight line with a smaller slope indicates the supplementary delignification phase. The average amount of lignin removed during the bulk delignification phase at 4 temperatures was 78.6%, accounting for 92.7% of the total amount of lignin, while 6.5% was removed in the supplementary delignification phase, which is 8.0% of the total amount of lignin.

Figure 2 shows that with the prolongation of cooking time, the ratio of delignification percentage to carbohydrate loss rate increases in the bulk delignification stage and decreases in the supplementary delignification stage. This indicates that lignin dissolution is the main process in the bulk delignification stage, accompanied by a small amount of carbohydrate degradation, while in the supplementary delignification phase, the percentage of carbohydrate dissolution increases and then becomes the main component. When the cooking liquor concentration and the cooking temperature are constant, proper prolongation of cooking time can result in the liquor completely soaking into the fiber of the raw materials, thus more thoroughly removing the lignin. However, if the cooking time is too long, the carbohydrates in the fiber raw materials will be more severely degraded, thus affecting the pulp yield and fiber strength. Therefore, excessive prolongation of the supplementary delignification period should be avoided as much as possible. This is similar to the conclusion of Epelde et al.,\(^ {30}\) who studied the delignification kinetics of wheat straw kraft and soda pulping and observed that approximately 90% of the lignin dissolved during the initial stage. Zhu and Qiao\(^ {31}\) used a microwave to cook wheat straw under atmospheric pressure, and the results showed that the delignification process was divided into a quick stage and a residual stage. Huang et al.\(^ {32}\) pointed out that the porous structure of rice straw in the study of cooking mechanisms and kinetics of \( \text{NH}_4\text{OH}-\text{KOH} \) indicated that the delignification rate of herbaceous plants was faster in the early stage of cooking.

In order to further analyze the degradation of carbohydrates during the entire cooking process, we calculated the loss ratios of cellulose and hemicellulose, using 90 and 100 °C as examples (see Figure 3). Figure 3 shows that with the two cooking temperatures, the loss ratios of cellulose and pentosan are significantly different with increasing cooking time periods. When the cooking time is less than 300 min, the cellulose loss ratio is less than 20%. When the cooking time exceeds 300 min, the cellulose loss ratio is significantly increased because hemicellulose and lignin have been largely degraded after this time. This indicates that cellulose is well-retained throughout the cooking process, unless the cooking time is excessively extended. The loss ratio of pentosan was high, mostly between 60 and 80% at 90 °C and more than 80% at 100 °C. Its comparison with the cellulose loss ratio clearly shows that the carbohydrate loss is mainly based on hemicellulose. This conclusion is consistent with the study of wheat straw by Ma et al.\(^ {33}\) and the study of poplar wood by Zhu et al.\(^ {27}\) using the same acid.

2.2. Kinetics of Delignification. In order to analyze the delignification kinetics and hemicellulose loss kinetics of rice straw more conveniently and effectively, we used a combined delignification factor (CDF) and a combined hydrolysis factor.

Figure 2. Ratio of delignification over carbohydrate loss. Note that the pulping conditions entailed the following: \( p \)-TsOH, 50% (w/w); liquor-to-solid ratio, 10:1; pulping time, 0–360 min; and pulping temperature, 70–100 °C.
(CHF) based on the reaction kinetics.\textsuperscript{27,33,34} Using a biphasic assumption,\textsuperscript{35} both pentosan and lignin contain a fast and slow fraction. Then, the fraction of pentosan, $X_R$, and lignin, $L_R$, that remained in pulp can be expressed as

\[
X_R = (1 - \theta - \theta_R)e^{-\text{CHF}} + \theta e^{-/\text{CHF}} + \theta R
\]

\[
\text{CHF} = \exp\left(\alpha - \frac{E}{RT} + \beta C\right)Ct
\]

\[
L_R = (1 - \theta' - \theta_R')e^{-\text{CDF}} + \theta' e^{-/\text{CDF}} + \theta R'
\]

\[
\text{CDF} = \exp\left(\alpha' - \frac{E'}{RT} + \beta'C\right)Ct
\]

where $C$ is the p-TsOH molar concentration (mol/L), $R = 8.314$ (J/mol/K) is the universal gas constant, $t$ is the reaction time in min, and $T$ is the reaction temperature in kelvin. $\alpha$, $\alpha'$, $\beta$, and $\beta'$ are adjustable parameters; $E$ and $E'$ are the apparent activation energy (J/mol); and $\theta$ and $\theta'$ are the initial fraction of slow-reacting xylan and lignin, respectively. $f$ and $f'$ are the ratios of the reaction rate between the slow and fast xylan and slow and fast lignin, respectively. Excellent fittings of the data of pentosan and lignin that remained in pulp were obtained, as shown in Figure 4. This indicates that as long as the required severity of the CHF or CDF is applied, the required hemicellulose dissolution rate or delignification level can be achieved without relying on a single reaction condition.\textsuperscript{27,29}

Therefore, it can be more convenient to achieve the desired result by adjusting the conditions, which would be performed during the process of scale-up. If $\theta_R$ and $\theta_R'$ are set to 0, the fitting parameters are listed in Table 1.

Table 1 shows that the activation energy of the hemicellulose loss reaction and delignification reaction was 68.21 and 46.05 kJ/mol, respectively. Experiments by Abdul-Karim et al.\textsuperscript{36} on kraft pulping kinetics of Hungarian wheat straw showed that the delignification process was a first-order reaction and the activation energy of the delignification reaction was 131 kJ/mol. Studies by Epelde et al.\textsuperscript{30} examined the delignification reaction mechanism and kinetics of kraft soda pulping of wheat straw. They demonstrated that the delignification reaction was first order to lignin and that the activation energy of the delignification reaction was 93 kJ/mol. Tong et al.\textsuperscript{37} discussed the reaction kinetics during the process of cooking, and the activation energy of delignification was 49.5 kJ/mol. Therefore, the activation energy of the delignification reaction of p-toluene sulfonic acid for rice straw pulping is much lower than that of alkali pulping.

Pulping with different organic solvents and p-toluene sulfonic acid pulping should also be compared. Dang and Nguyen\textsuperscript{38} determined that the activation energy for the ethanol–sulfuric acid cooking of wheat straw was 128 kJ/mol, and therefore, the activation energy for the delignification reaction of rice straw pulping by p-toluene sulfonic acid is still advantageous. In addition, it is necessary to compare straw with wood. Garland et al.\textsuperscript{39} studied the activation energy of 126 kJ/mol for *Eucalyptus diversicolor* wood alkaline pulping.
while studies on delignification kinetics of birch alkali pulping were conducted by Lindgren and Lindstrom and studies on ethanol autocatalytic pulping kinetics of *Eucalyptus globulus* by Oliet et al., and they all indicate that wood generally has a higher activation energy. Consequently, the activation energy of *p*-toluenesulfonic acid pulping was compared with that of other organic solvent pulping, and the activation energy of straw and wood was compared. These comparisons indicated that the *p*-TsOH pulping of rice straw is a method that is easily performed with low activation energy.

### 3. CONCLUSIONS

The delignification reaction of *p*-TsOH cooking can be divided into two phases, namely, the bulk delignification phase and the supplementary delignification phase. Lignin dissolution was the main process in the bulk delignification stage, accompanied by the degradation of a small amount of carbohydrates. In the supplementary delignification stage, the lignin delignification rate was low and carbohydrate degradation was severe. The degradation of carbohydrates is mainly based on the dissolution of hemicellulose. The degradation process of lignin and hemicellulose can be well-fitted using the CDF and CHF models. The activation energies of the hemicellulose loss reaction and delignification reaction were 68.21 and 46.05 kJ/mol, respectively. Therefore, *p*-TsOH pulping is a pulping technology with a very broad application prospect.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials

Rice straw was obtained from Suihua City, Heilongjiang Province, China, and it was cut into segments of 1–2 cm. Chemical analysis of the material indicated that it was composed of 74.22% holocellulose, 12.94% pentosan, 12.04% lignin, 10.91% ash, and 3.17% benzene alcohol extract. The purity of *p*-TsOH was approximately 96%.

#### 4.2. Pulping Process

The mass percentage concentration of *p*-TsOH solution used was 50%. The pulp yield and lignin content of unscreened pulp were determined by constant-temperature cooking at 50% concentration of *p*-TsOH aqueous solution and a 10 liquor-to-solid ratio. The pulp was cooked at 70, 80, 90, and 100 °C in a normal-pressure water bath for 10, 20, 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330, and 360 min.

#### 4.3. Evaluation of the Chemical Properties of the Pulp

The starting material and the products were characterized according to the following standard methods: holocellulose (GB/T 2677.10-1995), pentosan (GB/T 2677.9-1994), lignin (GB/T 2677.8-1994), ash (GB/T 2677.3-1993), and benzene alcohol extract (GB/T 2677.6-1994); the cellulose content was determined using the nitric acid–ethanol method.

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### Notes

The authors declare no competing financial interest.

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