



# Sulfite–formaldehyde pretreatment on rice straw for the improvement of enzymatic saccharification



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## HIGHLIGHTS

- Sulfite–formaldehyde (SF) was used as a pretreatment on rice straw.
- Fermentable sugars, lignin and silica can be separated by SF and enzyme treatment.
- Most glucan (90%) and xylan (72%) were retained with a lignin removal of 75%.
- Over 70% of the original polysaccharides can be converted into fermentable sugars.
- 78% of silica was kept in the residue after enzymatic hydrolysis.

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## ABSTRACT

Rice straw is one of the most abundant agricultural residues in China. It is considered as a promising raw material for bioethanol production. In this work, rice straw was pretreated by sodium sulfite–formaldehyde (SF) for improving enzymatic saccharification. The SF pretreatment, using proven technology and industrialized equipment, showed efficient delignification selectivity and high carbohydrates retention in pretreated solid. The highest sugar yields of 79.0%, 88.8% and 71.1% for total sugar, glucan and xylan, respectively were obtained at an enzyme loading of 40 FPU/g-substrate after the raw material pretreated with 12% sodium sulfite at 160 °C. About 75% of lignin was dissolved in pretreatment spent liquor and 78% of silica was retained in the residue of enzymatic hydrolysis. The results proved sulfite–formaldehyde as a promising pretreatment for the production of bioethanol as well as potential high value added by-products of silica nanoparticles and lignosulfonate.

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## 1. Introduction

Rice (*Oryza sativa* L.) straw as an agricultural residue is one of the most abundant annual renewable lignocellulosic resources in the world. Up to now rice straw is used as a source of livestock feed, organic fertilizer and pulping, however an increasing proportion of rice straw is burned in farm field which leads to energy waste, greenhouse gas emissions as well as air pollution (Kim and Dale, 2004). Recently, rice straw is attracting keen interest as a potential feedstock for bioethanol production since it contains high cellulose and hemicellulose that can be readily hydrolyzed into fermentable sugars (Binod et al., 2010). As FAO statistics in

2010, world production of rice is 696.3 million tons, this amount of rice can potentially produce 884.3 million tons rice straw or 371.4 billion liters bioethanol per year globally if the technology were available (Summers et al., 2003). However, technologies for developing second generation biofuels encounter great challenges due to the lower fermentable sugar yield.

Cellulose, hemicellulose and lignin are three major constituents of plant cell wall. The cellulose and hemicellulose are tightly packed in plant cell wall and surrounded by lignin, forming highly recalcitrant structures against direct enzymatic attack (Park et al., 2010). This is the major barrier to the economic development of non-food bioethanol production (Himmel et al., 2007). An effective pretreatment is in demand to remove lignin and sufficiently expose cellulose to achieve more fermentable sugar during enzymatic hydrolysis process (Ding et al., 2012; Mosier et al., 2005). Current existing efforts of pretreatment are focused on alkaline, dilute acid, steam explosion, ammonia, and organosolv pretreatment technologies that have achieved a certain degree of success (Alvira et al., 2010; Jin et al., 2010; Yang and Wyman, 2008). However,

Abbreviations: NMR, nuclear magnetic resonance; SD, standard deviation.

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these pretreatments have not been commercialized for various reasons.

The sodium sulfite–formaldehyde (SF) cooking was developed to selectively remove lignin and to keep high carbohydrates retention for sulfite pulping (He et al., 1994). As a pretreatment for enhancing enzymatic saccharification, SF cooking has several advantages to facilitate commercialization. Unlike acid or steam explosion pretreatment, it retains the most polysaccharides in pretreated straw for enzymatic hydrolysis and avoids collecting pentose in pretreatment step, resulting in dramatic high efficiency and low cost of fermentation process. In addition, SF pretreatment produces no toxic by-products such as furfural, acetic acid, and metal ions (from hemicellulose degradation) to affect the fermentation step and cause equipment corrosion. Furthermore, all the equipment and processes of SF pretreatment have been industrially practiced for decades in dozens of pulp mills in the world.

During SF pretreatment, the lignin is easily dissolved in spent liquor since sulfonation generates the hydrophilic group in the side chain of hydrophobic lignin polymer (Ohi et al., 1994). The addition of HCHO not only increases the pH value of cooking liquor but also improves the solubility of lignin by sulfomethylation occurred at C<sub>5</sub> position of lignin aromatic ring (Ohi et al., 1990). The carbohydrate yield of alkaline sulfite cooking is 1.5–2% higher than in the case of soda cooking at the same delignification degree (Ohi et al., 1989). Moreover, lignosulfonate, which can be recovered from the spent liquor of SF pretreatment, is recognized as the most potential commercial lignin derivative products. It has wide applications in dispersants of concrete, dyestuff and coal-water slurry, industrial binders, agricultural chemicals and floating chemicals etc. (Yan et al., 2010) due to its dispersive, stabilizing, binding and complexing properties. Therefore, SF pretreatment can use the existing industrial technology and equipment, and is easily to realize commercialization with low technological and environmental risks and barriers than other pretreatment approaches.

In this work, the effects of SF pretreatment with different Na<sub>2</sub>SO<sub>3</sub> charge and temperature on the chemical compositions of rice straw, as well as on the improvement of enzymatic saccharification were investigated, and the condition of SF pretreatment for bioethanol production was optimized.

## 2. Methods

### 2.1. Materials

Rice straw used as feedstock in this work was provided by a pulp mill in Jiangsu, China. Air dried rice straw without classification was cut into 3–5 cm in length, then collected in sealed plastic bags and stored at 4 °C in a refrigerator.

The main components of rice straw were analyzed. Prior to analysis, the rice straw was ground using a Wiley mill, then the particles size between 40 and 60 mesh were collected and extracted with benzene–ethanol (2:1, v/v) in a Soxhlet apparatus for 8 h. All the weight percentages were calculated based on the oven dry (od) samples.

The enzymes used in this work, cellulase (NS 50013), xylanase (NS 50014) and β-glucosidase (NS 50010) were provided by Novozymes (Franklinton, NC, USA). All the other chemicals were analytical grade and purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China) and used as received without further purification.

### 2.2. Sodium sulfite–formaldehyde pretreatment

A ten-bomb lab-scale pulping system with oil bath was used with batch capacity of 80 g od rice straw per bomb. Rice straw was directly subjected to SF pretreatment at 150 °C and 160 °C

for 1 h. Sodium sulfite and formaldehyde with a molar ratio of 1:1 were used as pretreatment chemicals, and anthraquinone was charged as additive to enhance lignin removal. The Na<sub>2</sub>SO<sub>3</sub> charge ranged from 4% to 16% (w/w), and the anthraquinone dosage was 0.1% (w/w) on the basis of untreated rice straw. The SF pretreated samples were expressed as SF T–S, in which T and S are pretreatment cooking temperature and Na<sub>2</sub>SO<sub>3</sub> charge, respectively. The ratio of cooking liquor to straw was 6 (v/w). The straw was first impregnated with the pretreatment liquor at 60 °C for 30 min. After impregnation, the temperature was raised with the rate of 2 °C/min to the target temperature and then maintained for 60 min. At the end of the pretreatment, the bombs were cooled in cold water to room temperature. The samples were filtered through cheese cloth. The original filtrates were collected for pH measurement. The remaining solid was washed with hot water to remove residual chemicals and dissolved straw compounds. The solid recovery was calculated according to the wet weight and moisture content of the collected solid.

### 2.3. Enzymatic hydrolysis

A laboratory disk refiner (Φ 300 mm, KRK, Jilin, China) was used for the defibration of the pretreated rice straw at 3000 rpm to produce substrate. Enzymatic hydrolyses of the substrate were carried out in a 250 mL Erlenmeyer flask with substrate consistency of 5% (w/w) at 50 °C using a shaking incubator (DZH-2102, Jinghong, Shanghai, China) at 180 rpm for 48 h. Sodium acetate buffer was used in the mixture to maintain the pH at 4.8, while 0.3% (w/v) sodium azide was added to inhibit the microbial infections. An enzyme cocktail mixed by NS 50013, NS 50014 and NS 50010 with a ratio of 1 FPU:1.2 FXU:1 CBU was used to hydrolyze the substrate. The activity loading was 5–40 FPU/g-substrate based on a cellulase charge. Enzymatic hydrolysis residue and hydrolysate was separated by centrifugation. Hydrolysates were sampled for monomeric sugar (glucose, xylose, galactose and arabinose) analysis. Each data point was the average of duplicate experiments.

### 2.4. Analytical methods

Cellulase activity of cellulase (NS 50013), in terms of “filter paper unit” (FPU) was determined by the filter paper method using Whatman No. 1 filter paper as a standard substrate (Ghose, 1987). Manufacturer specified activity of NS 50014 and NS 50010 was directly used to calculate loading.

The enzymatic hydrolysate was diluted 1000 times with the addition of L-(–)-fucose (F2252, Sigma, Saint Louis, MO) as an internal standard. Monosaccharides were determined using an improved high performance anion exchange chromatography (Dionex ICS-3000, Dionex Corp., Sunnyvale, CA) with pulsed amperometric detection (HPAEC-PAD) method. A CarboPac™ PA1 Analytical (2 × 250 mm) column and a CarboPac™ PA1 Guard (2 × 50 mm) (Dionex Corp., Sunnyvale, CA) were used as analytical and guard column, respectively. An 18 mmol/L NaOH solution prepared with degassed super-purified deionized water was used as eluent at a flow rate of 0.25 mL/min. Aliquots (5 μL) were injected after passing through a 0.22 μm nylon syringe filter. The column reconditioned using 200 mmol/L NaOH after each three analysis. The concentration of monosaccharide was corrected by calibration curve of standard sugars. The average of duplicate runs was used in reporting. Data of glucose, xylose, arabinose and galactose contents were corrected to anhydro units, i.e. glucan, xylan, arabinan and galactan for the calculation of sugar release and yield. Sugar release and sugar yield of enzymatic hydrolysis were calculated by the following equations.

$$\text{Sugar release (\%)} = \frac{\text{Sugar in enzymatic hydrolysate (g)}}{\text{Untreated rice straw (g)}} \times 100\%$$

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