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# Pretreating wheat straw by the concentrated phosphoric acid plus hydrogen peroxide (PHP): Investigations on pretreatment conditions and structure changes

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## HIGHLIGHTS

- PHP concurrently promoted hemicellulose and lignin removal from wheat straw.
- Hemicellulose was more sensitive to PHP than lignin, and followed by cellulose.
- Hemicellulose and lignin removal were intensified by increasing temperature and time.
- Higher H<sub>3</sub>PO<sub>4</sub> proportion was positive to remove hemicellulose, negative to delignin.
- 92–100% cellulose were recovered with glucose yield of 29.1–32.6 g/100 g wheat straw.

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## ABSTRACT

Wheat straw was pretreated by PHP (the concentrated H<sub>3</sub>PO<sub>4</sub> plus H<sub>2</sub>O<sub>2</sub>) to clarify effects of temperature, time and H<sub>3</sub>PO<sub>4</sub> proportion on hemicellulose removal, delignification, cellulose recovery and enzymatic digestibility. Overall, hemicellulose removal was intensified by PHP comparing to the concentrated H<sub>3</sub>PO<sub>4</sub>. Moreover, efficient delignification specially happened in PHP pretreatment. Hemicellulose removal and delignification by PHP positively responded to temperature and time. Increasing H<sub>3</sub>PO<sub>4</sub> proportion in PHP can promote hemicellulose removal, however, decrease the delignification. Maximum hemicellulose removal and delignification were achieved at 100% and 83.7% by PHP. Enzymatic digestibility of PHP-pretreated wheat straw was greatly improved by increasing temperature, time and H<sub>3</sub>PO<sub>4</sub> proportion, and complete hydrolysis can be achieved consequently. As temperature of 30–40 °C, time of 2.0 h and H<sub>3</sub>PO<sub>4</sub> proportion of 60% were employed, more than 92% cellulose was retained in the pretreated wheat straw, and 29.1–32.6 g glucose can be harvested from 100 g wheat straw.

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## 1. Introduction

With the increasing in global energy demands and warming concerns caused by traditional fossil fuels, seeking an alternative and renewable energy from various biomass is attractive, in which refining biofuels from biomass is of particular interest (Xin et al., 2015). Currently, bioethanol is a dominating biofuel for transportation with an annual world production increasing from 28.5 billion

liters in 2004 to 87.2 billion liters in 2013, in which sugar (starch)-based biomass for bioethanol production occupied greatly (Ajanovic, 2011; Nair et al., 2015). In contrast to the sugar (starch)-based biomass, lignocellulosic feedstocks, such as agricultural residues, forestry wastes, and grasses, are considered to be promising sources for bioethanol in future due to their renewability, wide distribution, abundance, and rich in polysaccharides (Rubin, 2008; Sanchez et al., 2015). However, it has already been confirmed that the nature recalcitrance of lignocellulosic biomass hindered the potential application on bioethanol conversion. Especially, hemicellulose and lignin actually acted as physical barriers restricting the accessibility of enzymes to cellulose (Zakaria

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et al., 2015). Therefore, lignocellulosic feedstocks have to be pretreated to break the nature recalcitrance and remove the barriers of hemicellulose and lignin for improving enzymatic hydrolysis and maximizing fermentable sugar yield.

Many pretreatment technologies have been widely investigated on various lignocellulosic feedstocks. Their characteristics were systematically summarized and overviewed in many review articles indicating that the investigated pretreatment technologies displayed some distinguished functions to decrease the nature recalcitrance. The typical physical pretreatments, including mechanical comminution and extrusion, are believed to reduce particle size and cellulose crystallinity for increasing the specific surface, and disrupt lignocellulose structure for defibrillation, fibrillation and shortening the fibers (Alvira et al., 2010). As some leading physico-chemical pretreatments, steam explosion, liquid hot water, and ammonia fiber explosion have been popularly investigated up to now, in which steam explosion and liquid hot water are markedly characterized by hemicellulose degradation or solubilization (Pérez et al., 2008; Pan et al., 2005). Ammonia fiber explosion can decrease cellulose crystallinity and disrupt lignin–carbohydrates linkages, although little hemicellulose and lignin can be removed (Laureano-Perez et al., 2005; Wyman et al., 2005). As the most investigated chemical pretreatments, alkali-involved pretreatments exhibit the efficient lignin solubilization and cellulose swelling in room temperature. Unlike alkali-involved pretreatments, acid-involved pretreatments are always performed at relatively high temperatures using various diluted-acids, by which the hemicellulose fraction can generally be solubilized (Alvarez-Vasco et al., 2014; De Vasconcelos et al., 2013). Besides, the organosolv and ozonolysis methods are another well-investigated chemical pretreatments, which typically functions as delignification by solubilization and oxidation (García-Cubero et al., 2009; Zhao et al., 2009). Recently, solvent-based pretreatments have received many attentions as they can greatly increase cellulose accessibility by cellulose regeneration at moderate conditions comparing with the above mentioned pretreatments (Sathitsuksanoh et al., 2013). The representative solvents for cellulose are generally reported as ionic liquids, concentrated  $H_3PO_4$ , N-Methyl-Morpholine-N-Oxide (N-MMO), Urea/NaOH, and N,N-Dimethylacetamide (DMAC)/LiCl<sub>2</sub> (Wang et al., 2011). By contrast, the concentrated  $H_3PO_4$  is a better solvent, and can be employed for pretreating lignocellulosic feedstocks at gentle temperatures, in which hemicellulose removal is a typical feature (Zhang et al., 2007). However, lignin cannot be greatly removed by the concentrated  $H_3PO_4$ , and the improvement on the cellulose digestibility thereby was finite (Wang et al., 2014). In order to enhance the oxidizability of the concentrated  $H_3PO_4$ ,  $H_2O_2$  was supplemented in the concentrated  $H_3PO_4$  for pretreating various typical feedstocks, such as agricultural residues, grassy biomass, softwood, hardwood, bamboo residues and their mixtures, at 50 °C. Delignification was greatly improved as expected, and hemicellulose removal was also achieved efficiently (Wang et al., 2014). Nevertheless, the in-depth investigations on hemicellulose removal, delignification and cellulose digestibility as affected by pretreatment conditions are not available currently, which not only affects glucose yield from cellulose, but also relates to the potential utilization of hemicellulose and lignin.

As one of the most abundant agriculture residues, wheat straw was selected as a model feedstock for PHP (the concentrated phosphoric acid plus hydrogen peroxide) pretreatment to investigate the effects of some main pretreatment conditions, including temperature, time and  $H_3PO_4$  proportion. Based on the main composition of the pretreated wheat straw, hemicellulose removal, delignification and cellulose recovery were analyzed to clarify their responses to the mentioned pretreatment conditions. Correspondingly, enzymatic hydrolysis of the pretreated wheat

straw was evaluated to check their digestibility responses to the pretreatment conditions. Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) were employed to assess the structure changes as affected by PHP pretreatment.

## 2. Methods

### 2.1. Lignocellulosic feedstock

Wheat straw was collected from the farm of Sichuan Agricultural University, Chengdu, China. The collected straw was air-dried, and milled through a 40 mesh sieve ( $\leq 0.45$  mm) prior to pretreatment. Main chemical composition of wheat straw was as follows: cellulose of 31.6% (represented by glucan content), hemicellulose of 16.2% (represented by xylan content), acid-insoluble lignin of 18.5%, acid-soluble lignin of 2.7%, ethanol-extractives of 13.3%, and ash of 3.9%.

### 2.2. Pretreatment

PHP pretreatment was carried out in a 250 mL serum bottle with 8.0 g wheat straw (dry basis) and 80.0 g PHP mixture. The bottle was sealed by a rubber stopper and hooped using an aluminum-seal. The sealed bottles were shaken in an orbital shaker with 100 rpm for pretreatment. Afterwards, pretreatment was ceased by dilution using 5 folds distilled water (450 mL). The pretreated wheat straw was washed by distilled water and dewatered using a dewatering centrifuge till the pH was higher than 5.5. The washed substrates were stored in a freezer ( $< -18$  °C) for further analysis and enzymatic hydrolysis. Pretreatment temperature and time were investigated in range of 10–50 °C and 1.0–5.0 h, respectively. The  $H_3PO_4$  proportions of 50–80% (w/w) in PHP mixture were discussed as well (the corresponding  $H_2O_2$  proportion in PHP was 12.35–1.77%). In addition, the comparative pretreatment by only  $H_3PO_4$  was performed with the similar procedure.

### 2.3. Enzymatic hydrolysis

Cellulase (Celluclast 1.5 L) from *Trichoderma reesei* ATCC26924 (Purchased from Sigma-Aldrich Co., Ltd, USA) supplemented with cellobiase (Novozyme 188) (Purchased from Sigma-Aldrich Co., Ltd, USA) was employed for enzymatic hydrolysis. The labeled activities of cellulase and cellobiase were 700 FPU·g<sup>-1</sup> and 250 IU·g<sup>-1</sup>, respectively. The pretreated wheat straw was enzymatically hydrolyzed in acetate buffer (0.05 M, pH 5.0) with solid fraction of 2.0% (w/v, dry basis). Cellulase and cellobiase were loaded as 20 FPU·g<sup>-1</sup> glucan and 40 IU·g<sup>-1</sup> glucan, respectively. All runs of hydrolysis were performed in duplicate in 150 mL screw flasks with 20 mL working volume, and the flasks were shaken at 50 °C in an incubator with 150 rpm for 72 h. 0.1 mL tetracycline (40 mg·L<sup>-1</sup>) was added prior to the hydrolysis to inhibit the microorganisms that may potentially consume the fermentable sugars. 800  $\mu$ L hydrolysate was periodically sampled during hydrolysis and boiled for 10 min to deactivate the enzymes and centrifuged at  $1.3 \times 10^5$  rpm, 4 °C for 10 min. The supernatant was stored in the freezer ( $< -18$  °C) for glucose determination.

### 2.4. Analytical methods

The unpretreated and pretreated wheat straw were analyzed for Klason insoluble lignin and carbohydrates according to the method in the Tappi-T-22 om-88. The hydrolysate from the Klason analysis was retained and analyzed for acid-soluble lignin by an UV spectrophotometer at 205 nm. Glucose and xylose in the hydrolysate

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