



The impact of glycerol organosolv pretreatment on the chemistry and enzymatic hydrolyzability of wheat straw



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HIGHLIGHTS

- Glycerol organosolv pretreatment (GOP) improves substrate hydrolyzability effectively.
- The mechanism was elaborated with analysis at macro-, micro- and nano-levels.
- GOP can drive concurrently the lignocellulosic and vegetable oil bio-refinery.
- New insights provide reference for optimization and scale-up of the GOP process.

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ABSTRACT

Given that the glycerol organosolv pretreatment (GOP) can effectively improve the hydrolyzability of various lignocellulosic substrates, physicochemical changes of the substrate before and after the pretreatment was characterized to elucidate what is responsible for it. The effect of GOP on the main components and hydrolyzability of wheat straw was revisited. Results demonstrate that the GOP should be a promising candidate for the current pretreatment. Then the composition and structure of substrates was measured at multi-dimensional scales by using various analytic equipment such as TGA, SEM, AFM, CLSM, FT-IR, XRD and solid-state CP/MAS ¹³C NMR. This paper reports some new insights on the mechanism behind that, which can be beneficial for further development, optimization, and scale-up of the GOP process.

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1. Introduction

The transition from a traditional “oil-refinery” to a “bio-refinery” based on renewable lignocellulosic biomass is crucial if we are to move to a more environmentally friendly economy (Rubin, 2008). In order to make these bio-based products more cost-competitive with fossil-derived conventional commodities, an efficient pretreatment strategy is needed to first open-up/disrupt the complex plant cell wall structure, which allows the “cellulase” enzymes to access and deconstruct the polysaccharides within the biomass into a monomeric sugar platform (Himmel et al., 2007). An ideal pretreatment approach should be not only

economically feasible but also able to fractionate and recover most of the major chemical components (i.e., cellulose, hemicellulose, and lignin) in the useable form (Lynd et al., 2008). Although numerous potential pretreatment strategies such as acid/alkaline, steam explosion and ammonia fiber explosion (AFEX) pretreatments have been exclusively studied, these present pretreatment techniques are still encountered with various drawbacks especially for the inefficient use of biomass lignin (Kumar et al., 2009; Chundawat et al., 2011).

Organosolv pretreatment, on the other hand, has addressed lots of attention due to the efficiency of fractionating the biomass components and the potential of scale-up in the commercially relevant bio-refinery process (Hallac et al., 2010; Sannigrahi et al., 2010; Zhao et al., 2009). The conventional organosolv pretreatment is referred to process with some low boiling-point organic solvents, as such ethanol, methanol, acetone, formic acid and acetic acid.

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Especially the ethanol organosolv pretreatment developed by Pan et al. (Pan et al., 2005, 2006, 2007) from the Alcell® pulping process and Lignol process is typical of the process. The organosolv fractionation has been considered to be a promising biorefinery approach given the coproduction of cellulose products (e.g., fibers or enzymatically digestible cellulose), high-purity lignin and hemicellulose-derived products such as xylose, furfural and acetic acid (Zhao et al., 2009). Organosolv lignin with its relatively low molar mass, high purity and abundance of reactive groups is a preferred candidate for phenolic resins. However, the low-boiling-point organic solvents used in the pretreatment process have been restricting the process development because of the high pressure operation as well as their high volatility and flammability (Sun and Chen, 2007, 2008). In addition, the cost of these solvents is usually too high to be industrially relevant. Therefore, it becomes crucial to identify a high-boiling-point organic solvent with a low price for developing an efficient organosolv pretreatment process.

Glycerol, a high-boiling-point organic solvent derived from the oleochemicals industry as the byproduct, has become very attractive. Recently, the soaring petroleum price has made the oleochemicals industry, especially for biodiesel production, more flourishing, which has driven the glycerol market oversupplied. Although there is an extensive utilization in food, cosmetic and pharmaceutical industry for high purity (>99.5%) of glycerol, it is still very challenging to purify and utilize it. Hence, a huge amount of industrial glycerol waste is expected on the market, which might affect the sustainability of the biodiesel industry. In this context, it is important to find some value added applications for the industry glycerol waste.

Initially, Demirbas and his colleagues (Kucuk and Demirbas, 1993; Demirbas, 1998) studied an alkaline-catalyzed glycerol organosolv pulping of the wood chips. Based on the glycerol organosolv pulping process, an atmospheric aqueous glycerol autocatalytic organosolv pretreatment (AAGAOP), which is using the industrial glycerol derived from oleochemical industry, was initiated in our lab (Sun and Chen, 2007, 2008). Thereafter, numerous research groups have tested the GOP on various lignocellulosic biomass (Martin et al., 2011; Novo et al., 2011; Zhang et al., 2013a; Guragain et al., 2011; Saberikhah et al., 2011; Hundt et al., 2013a,b; Romani et al., 2013), with/without an acid/alkaline catalyst and have also confirmed that the pretreatment is indeed an effective process to improve the hydrolyzability of lignocellulosic substrates. However, most of these present literatures have been focusing on the enhancement of enzymatic hydrolysis of the glycerol organosolv pretreated substrates, without assessing physico-chemical changes of the substrate that contributed to the significantly improved substrate hydrolyzability (Sannigrahi et al., 2010). Therefore, it's important to better understand the effects of GOP on the substrate properties in order to further the development, optimization, and scale-up of this pretreatment process.

Accordingly, the objective of this study is to investigate the effect of AAGAOP on the biomass physicochemical properties in order to better elucidate the mechanism behind the significantly improved substrate hydrolyzability. Based on our previously developed AAGAOP process, the substrates before and after pretreatment were characterized and compared at multi-dimensional scales with various modern analytic equipment. Briefly, the scanning electron microscopy (SEM), atomic force microscopy (AFM) and confocal laser scanning microscopy (CLSM) were applied to map the substrate morphological change, while the thermogravimetric analysis (TGA), Fourier Transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and solid-state cross-polarization magic angle spinning Carbon-13 nuclear magnetic resonance (CP/MAS ^{13}C NMR) were used to characterize the chemical compositional and physical structural changes. In addition, the solid-state

CP/MAS ^{13}C NMR was also employed to reflect the cellulose supermolecular structure of pretreated wheat straw (Chundawat et al., 2011; Ding et al., 2012). The susceptibility of pretreated substrates towards the enzymatic saccharification process was correlated by the changes of substrate physical and chemical properties.

2. Methods

2.1. Materials

Wheat straw was obtained from Henan Province, China. It was manually cut into scraps approximately 15 mm in length, dried to constant weight at 60 °C and then stored in the polyethylene plastic container. The resulting fiber fractions were also dried at 60 °C to a constant weight for dried weights determination, the content of three main components and enzymatic hydrolysis. The average main components (% w/w) of wheat straw, as determined by three replicate analyses, were as follows: 43.3% cellulose, 31.7% hemicelluloses and 17.3% lignin. All repetitive experiments were performed under the same condition and average values were reported. The standard deviations were less than 3.7%.

Industrial glycerol was of commercial grade (95% purity), purchased from a chemical plant in Jiangsu Province, China. It was diluted to 70% for use in the experiment. Cellulase GC-220 (FPA, 77.85 FPU/mL) was presented from Genencor Company in Jiangsu Province, China.

2.2. AAGAOP pretreatment of wheat straw

In the previous work, a simple set-up was designed and used in the laboratory. And the AAGAOP established the optimum experimental conditions as 220 °C for 3 h, with a liquid–solid ratio 200 g/10 g (Sun and Chen, 2008). Based on this, for a typical run, 10 g of dry wheat straw was suspended in 200 g of 70% aqueous glycerol. In the three-necked round bottom flask, a condenser was fitted in the right neck of the flask to reflux and the thermocouple wire was passed through the left neck to measure temperature, a stirrer was fitted in the middle neck of the flask to make the mixture stir fully. In order to avoid the formation of excessive foam, the sample was heated slowly so that the desire temperature was reached in approximately 40 min. The temperature was kept at 220 °C for 3 h and then allowed to cool. When the slurry had cooled to 120–130 °C, it was supplemented slowly with 200 mL of recycled industrial glycerol liquor (approximately 40% consistency) and stirred vigorously to disintegrate the fiber. After thorough disintegration, the insoluble solid fraction was separated by filtration through a G3 glass filter (100 mL, pore size 15–50 μm) and washed twice with 400 mL recycled industrial glycerol liquor. After thorough washing with tap water, the resulting solid ('pretreated' wheat straw) was divided into two parts. One part was conserved in a sealed bag at 5 °C for the subsequent enzymatic hydrolysis, and the other was dried at 60 °C to determine the pretreatment yield and components, and to characterize the structural change.

The filtrate was treated for recycling. After precipitation overnight at room temperature, the spent liquor was centrifuged at 4000 rpm for 30 min. The supernatant was used directly as recycling liquor for washing, i.e. recycled industrial glycerol liquor (approximately 40% consistency).

2.3. Enzymatic hydrolysis of the resulting fiber fractions

Each individual sample, equivalently at 0.5 g dry weight, of the wet solid fiber fraction from the pretreatment process was put into a 100 mL flask and suspended quickly with 25 mL acetate buffer (0.05 M, pH4.8) to acquire 25.5 g slurry with 2% solids (w/v) to

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