



Effects of acid and alkali promoters on compressed liquid hot water pretreatment of rice straw



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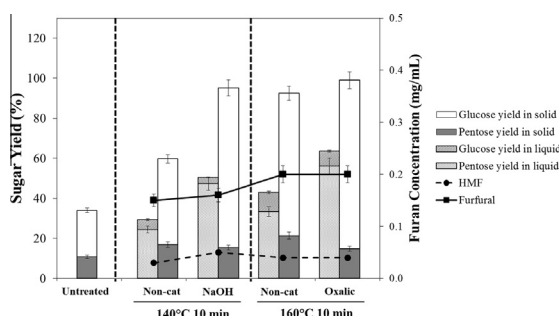
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HIGHLIGHTS

- Effects of promoters on efficiency and selectivity of LHW were studied.
- Promoters enhanced hemicellulose hydrolysis and digestibility of cellulose.
- Alkaline showed more pronounced effect at low LHW temperature compared to acids.
- Oxalic acid was a superior promoter in LHW leading to 91.2% glucose recovery.
- Effects of promoters to physicochemical changes of biomass were analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, effects of homogeneous acid and alkali promoters on efficiency and selectivity of LHW pretreatment of rice straw were studied. The presences of acid (0.25% v/v H₂SO₄, HCl, H₃PO₄, and oxalic acid) and alkali (0.25 w/v NaOH) efficiently promoted hydrolysis of hemicellulose, improved enzymatic digestibility of the solids, and lower the required LHW temperature. Oxalic acid was a superior promoter under the optimal LHW conditions at 160 °C, leading to the highest glucose yield from enzymatic hydrolysis (84.2%) and the lowest formation of furans. Combined with hydrolyzed glucose in the liquid, this resulted in the maximal 91.6% glucose recovery from the native rice straw. This was related to changes in surface area and crystallinity of pretreated biomass. The results showed efficiency of external promoters on increasing sugar recovery and saving energy in LHW pretreatment.

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1. Introduction

Lignocellulosic biomass is considered as a potential resource for production of biofuels, commodity chemicals and valorized

bio-products in the biorefinery industry, providing a more sustainable alternative platform industry to the current petrochemical-based production (Menon and Rao, 2012). Lignocellulose comprises three major constituents: (i) cellulose, a linear homopolymer of D-glucose formed into a highly organized crystalline fibrous structure; (ii) hemicellulose, an amorphous branched heteropolymer of pentoses, hexoses, and sugar acids, which acts

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as an interconnecting substance; and (iii) lignin, a heteropolymer of phenolic subunits, which acts as a protective shield giving strength to plant cells (Fengel and Wegener, 1984). Altogether, this complex structure makes lignocellulose highly resistant to chemical and enzymatic decomposition. Pretreatment represents an essential step to increase biomass digestibility in sugar platform biorefinery. Several chemical, thermal, and biological pretreatment methods have been extensively studied in order to increase susceptibility of the lignocellulose matrix to subsequent enzymatic hydrolysis (Kumar et al., 2009). The major effects of pretreatment include solubilization of hemicellulose and/or lignin, decrystallization of cellulose, reduction of degree of polymerization, and increase in accessible surface area. These changes in the lignocellulose matrix enhance enzyme hydrolytic efficiency and conversion yield (Van Dyk and Pletschke, 2012).

Liquid hot water (LHW) is a hydrothermal pretreatment method that is considered one of the most potent pretreatment technologies in terms of technical and economic aspects (Kruse and Dinjus, 2007). In this process, water is used as the sole reaction medium with no external chemical additives. Under elevated temperature (160–240 °C) and pressurized conditions (5–20 bars), the superheated liquid water auto-ionizes into hydronium ions which act as a promoter for cleavage of ester bonds of acetyl side chains of hemicelluloses, which results in formation of acetic acid (Teo et al., 2010). The *in situ* generated acid then autocatalyzes hydrolysis of the hemicellulose and alteration of lignin structure, leading to increased enzyme accessibility to the cellulose fibers. Compared with other thermochemical pretreatments such as steam explosion, LHW has the advantages of producing less by-products inhibitory to ethanologens and lower energy requirement (Ang et al., 2013). The majority of hemicellulose is retained in oligomeric and monomeric forms in the liquid fraction after LHW pretreatment (Ruiz et al., 2013). Non-catalytic LHW has been shown to be an effective pretreatment method for several agricultural by-products, including sugarcane bagasse, rice straw, corn stovers, and palm wastes (Laser et al., 2002; Imman et al., 2013).

Several homogeneous acids and alkalis have been used as external promoters in various hydrothermal pretreatment methods. The use of promoters allows for a reduction in reaction severity of the pretreatment conditions (temperature and time) without compromising pretreatment efficacy, and thus leads to improvements in overall process efficiency and economics (Kamm et al., 2013). Dilute mineral acids, particularly sulfuric acid and hydrochloric acid (Qin et al., 2012) are commonly used to increase solubilization of the hemicellulose fraction and biomass porosity. Weaker biomimetic acids such as oxalic and maleic acids can also function as external acid promoters with the advantage of less formation of inhibitory by-products from sugar degradation (Scordia et al., 2011). Furthermore, alkalis e.g. sodium hydroxide, ammonia, and lime can act as promoters in hydrothermal processes by inducing delignification of lignocellulosic biomass, with the same effect of improving digestibility of the biomass from pretreatment with lower energy expenditure.

In order to explore the use of external promoters on LHW, this study reports a comparison of different homogeneous acids and alkalis on catalytic LHW pretreatment of rice straw under pressurized water conditions aiming to enhancing hemicellulose hydrolysis and improving cellulose digestibility which reflected in greater sugar recoveries in the liquid and saccharified solid phases. Changes in biomass physicochemical characteristics, enzymatic digestibility of the pretreated biomass and sugar recovery from hemicellulose hydrolysis were investigated under different LHW conditions employing different promoters. The work shows potential of external promoters for promoting efficiency of LHW pretreatment of lignocelluloses for further conversion to valorized products in sugar platform biorefinery.

2. Methods

2.1. Raw material

Rice straw was collected from a local field in Pathum Thani province, Thailand. The biomass was physically processed using a cutting mill (Retsch SM 2000, Hann, Germany) and sieved to particles of size 250–420 μm (0.21–0.35 mesh). The processed biomass was then used as a starting material for experimental studies. The native rice straw used in this study contained 35.8% cellulose, 21.5% hemicellulose, and 24.4% lignin as the major constituents with a high ash content of 15.0% composed mainly of silica according to the standard NREL method (Sluiter et al., 2008).

2.2. Liquid hot water pretreatment

The pretreatment process was studied in a stainless steel reactor (2.5 cm diameter and 37.5 cm in length with the wall thickness of 2 mm and the total volume of 50 mL). The individual reactor vessel was installed with a thermocouple to measure the actual temperature inside the reactor. The standard reaction contained 2 g of rice straw and 20 mL of distilled water alone (uncatalyzed control), or supplemented with 0.25% (v/v) acid (H_2SO_4 , H_3PO_4 , HCl, and oxalic acid) or 0.25% (w/v) alkali (NaOH) as a promoter. Nitrogen was flowed into the reactor for purging and adjusting the initial pressure to 20 bars. The reactors were placed in furnace slots in a reactor system consisting of a 6 \times 50 mL-reactor in a temperature-controlled jacket equipped with a vertical shaking system to provide optimal mixing. The reaction was co-heated to 140–180 °C for 5–20 min. The reaction was quenched in a water bath after heating under the desired conditions. The solid cellulose fraction was separated by filtration on filter paper using a Buchner funnel and washed with distilled water and dried at 60 °C before subjecting to enzymatic hydrolysis. The liquid fraction was collected for analysis of sugar and inhibitory by-products by HPLC. The pretreatment reactions under each condition were performed in triplicate.

2.3. Enzymatic hydrolysis

The pretreatment efficiencies were assessed based on digestibility of the pretreated solid residues using a commercial enzyme mixture. The hydrolysis reactions of 1 mL total volume contained 5% (w/v) pretreated substrate with 10 FPU/g *Trichoderma reesei* cellulase (Celluclast™ 1.5 L, Novozymes AS, Bagsvaerd, Denmark) supplemented with 330 IU/g *Aspergillus niger* β -glucosidase (Novozym 188, Novozymes AS) and 120 IU/g hemicellulases (based on the endo-xylanase activity of *Humicola insolens* hemicellulase; Optimash® BG, Danisco AS, Copenhagen, Denmark) in 50 mM sodium acetate buffer, pH 5.0. The reactions were incubated at 50 °C for 72 h with vertical mixing at 30 rpm. The experiments were done in triplicate. Polysaccharide degrading activities were analyzed based on the amount of liberated reducing sugars using the 3, 5-dinitrosalicylic acid (DNS) method (Miller, 1959). Cellulase activity according to Filter paper unit (FPU) definition was analyzed according to a standard method (Adney and Baker, 1996). β -Glucosidase activity was determined using *p*-nitrophenyl- β -D-glucopyranoside as the substrate (Harnpicharnchai et al., 2009). One international unit (IU) was defined as the amount of enzyme which produced 1 μmole of reducing sugar or *p*-nitrophenolate in 1 min under the experimental conditions.

2.4. Analytical methods

The profile of sugars and inhibitory by-products (5-hydroxymethyl furfural and furfural) in the enzymatic hydrolyzates and

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