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Laboratory and pilot scale pretreatment of sugarcane bagasse by acidified aqueous glycerol solutions

Zhanying Zhang [a,b,*], Heng H. Wong [b], Peter L. Albertson [b], William O.S. Doherty [b], Ian M. O'Hara [a,b]

[a] Syngenta Centre for Sugarcane Biofuels Development, Queensland University of Technology, Brisbane, Australia
[b] Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane, Australia

HIGHLIGHTS

- Pretreatment with acidified glycerol solutions was evaluated at laboratory scale.
- Pretreatment was further evaluated at pilot scale.
- Pretreatment effectiveness at pilot scale was comparable to that at lab scale.
- Glycerol-glycosides were likely produced during pretreatment.
- Glycerol chlorination occurred during pretreatment with HCl as catalyst.

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ABSTRACT

Pretreatment of sugarcane bagasse with acidified aqueous glycerol solution was evaluated at both laboratory and pilot scales. Laboratory scale pretreatment (4.00 g dry mass in 40.00 g liquid) with glycerol solutions containing $\leqslant$20 wt.% water and 1.2 wt.% HCl at 130 °C for 60 min resulted in biomass having glucan digestibilities of $\geqslant$88%. Comparable glucan enzymatic digestibility of 90% was achieved with bagasse pretreated at pilot scale (10 kg dry mass in 60 kg liquid) using a glycerol solution containing 0.4 wt.% HCl and 17 wt.% water at 130 °C for 15 min. We attribute more efficient pretreatment at pilot scale (despite shorter reaction time and reduced acid content) to improved mixing and heat transfer in a horizontal reactor. Pretreatment of sugarcane bagasse with acid-catalysed glycerol solutions likely produces glycerol-glycosides, which together with hydrolysed lignin are potential substrates for the production of biopolymers.

1. Introduction

Lignocellulosic biomass consists of three major components: cellulose, hemicellulose and lignin. Due to the recalcitrance of lignocellulosic biomass, pretreatment is a prerequisite for the efficient enzymatic hydrolysis of cellulose and hemicellulose into fermentable sugars. So far, a variety of pretreatment methods including physical, chemical, biological and combined methods have been developed (Hendriks and Zeeman, 2009). Among these methods, glycerol-based pretreatment methods seem promising because of the low solvent cost and the high pretreatment effectiveness.

Glycerol is a non-toxic, high boiling-point (290 °C) organic solvent that is produced as by-product in large quantities from biodiesel factories (da Silva et al., 2009). The total annual production of glycerol in Europe during 2010 was estimated to be around 1.2 million tonnes (Behr et al., 2008) and the increasing production of biodiesel has significantly reduced the price of industrial-grade glycerol, which is currently ~US $500/tonne. Glycerol has been used as a standalone solvent, or in combination with alkaline catalysts such as Na_2CO_3 and NaOH, for the liquefaction (Demirbas, 2008, 2010), delignification (Demirbaş, 1998; Demirbaşa and Celikb, 2005; Küçük, 2005; Novo et al., 2011), and pretreatment of lignocellulosic biomass (Sun and Chen, 2007, 2008a). For example, delignification of sugarcane bagasse using 80% aqueous glycerol at 198 °C for 2.5 h removed up to 81% of lignin (Novo et al., 2011) while alkaline-catalysed glycerol pretreatment of wood biomass at 225 °C for 9 h removed ~88% of lignin and ~90% of hemicellulose (Demirbaş, 1998). However, in neither case was the susceptibility of the resulting delignified biomass to cellulases reported. Pretreatment of wheat straw with aqueous glycerol at 220 °C for 3 h without catalyst removed ~70% of hemicellulose and 65% of lignin while retaining 98% of cellulose and resulting in a enzymatic glucan digestibility of ~90% (Sun and Chen, 2008a).

Pretreatment or delignification of lignocellulosic biomass using glycerol or alkaline glycerol typically requires long reaction times (>2 h) and/or high reaction temperatures (>195 °C). Recent

* Corresponding author. Address: GPO Box 2432, 2 George St., Brisbane, QLD 4001, Australia. Tel.: +61 7 3138 7792; fax: +61 7 3138 4132.
E-mail address: jan.zhang@qut.edu.au (Z. Zhang).

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laboratory scale studies, although limited, showed that acidified glycerol solutions were also good solvents for pretreatment of lignocellulosic biomass and generate material with high glucan enzymatic digestibility (Liu et al., 2010; Martin et al., 2011). Pretreatment of sugarcane bagasse at 190 °C for 60 min with 80 wt.% glycerol and 0.94 wt.% H_2SO_4 resulted in a glucan enzymatic digestibility of greater than 90% (Martin et al., 2011). Microwave irradiation of Japanese cedar in acidified aqueous glycerol solution (containing 10 wt.% water) at 180 °C for 6 min with 0.1 wt.% HCl as catalyst resulted in a total sugar yield of 53.1% based on the original weight of a softwood biomass (Liu et al., 2010). It is worth noting that these studies did not include characterisation of the hydrolysates generated during pretreatment. Characterisation of pretreatment hydrolysates can provide useful data for the development, optimisation, and scale-up of pretreatment processes. Importantly, to date, the pretreatment of lignocellulosic biomass at the pilot scale using acidified glycerol has not been reported.

In the present study, sugarcane bagasse was pretreated at both the laboratory and pilot scales using acidified aqueous glycerol with HCl as the catalyst. Laboratory scale pretreatments were conducted in 100 mL flasks (with 4.00 g dry bagasse/flask) to assess the effects of acid content, time, water content and temperature on pretreatment effectiveness (glucan digestibility). Pilot scale pretreatment was conducted in a 150 L horizontal reactor (Andritz, USA) with a processing capacity of 10.0 kg dry bagasse/batch. The results demonstrated that pretreatment effectiveness at the pilot scale was similar or superior to pretreatment at the laboratory scale, although biomass particle size, biomass loading and water content were increased and pretreatment time was reduced. Characterisation of pretreatment hydrolysates at both scales provided evidence for glycerol chlorination with HCl as the catalyst. The results also indicated the presence of glycerol-glycosides (glycerol-xylosides and glycerol-glucosides) in the hydrolysates.

2. Methods

2.1. Materials

Sugarcane bagasse was provided by Racecourse Sugar Mill (Mackay, Australia). For pilot scale pretreatment, bagasse was used directly as received, which had a moisture of ~50 wt.%. For laboratory scale experiment, bagasse was washed with copious amounts of water, air-dried to constant weight, and milled in a Retsch® SM100 hammer mill (Retsch GmBH, Germany). The milled bagasse was screened using sieves and bagasse powder with particle sizes between 250 and 500 μm was collected and stored at room temperature (24 °C) in a sealed container. The moisture content of the bagasse powder was 6.9 wt.%. Glycerol (⩾99.7 wt.%) was purchased from Bronson and Jacobs Pty Ltd. (Australia). Hydrochloric acid (32 wt.%) was purchased from Merck Pty Ltd. (Australia). Accellerase™ 1000 (Batch No. 1600877126) was a Danisco product (Genencor Division, Danisco Inc., US) and was purchased through Enzymes Solutions Pty Ltd. (Australia). The filter paper activity of Accellerase™ 1000 was approximately 40 FPU/mL.

2.2. Pretreatment

2.2.1. Laboratory scale pretreatment

Laboratory scale pretreatments were conducted in a 100 mL glass flask. The flask had 4.30 g bagasse (4.00 g dry fibre), 39.70 g of glycerol solution containing the required amounts of acid and water and a magnetic stirrer with a specification of 3.0 cm (length) × 0.8 cm (width). The biomass loading (solid mass/liquid mass) was 10%. The flask was sealed to prevent water loss and immersed in a silicone oil bath preheated to the required temperature. The heating element was equipped with a magnetic stirring device (Ika Labortechnik, Germany). Pretreatment was carried out with a magnetic agitation speed set at 500 rpm. Following pretreatment, 40 mL of distilled water was added to the reaction mixture. The solution was mixed and filtered (Whatman 541 filter paper) to collect the pretreated bagasses. All the pretreatments were conducted in duplicate.

The filtrate was collected and stored at −20 °C for further analysis. The pretreated bagasse sample was washed with a total of 1.6 L of distilled water (400 mL/wash). A portion of the filtered, pretreated bagasse sample was rapidly frozen in liquid nitrogen and freeze-dried under vacuum. The dried sample was stored for compositional analysis and imaging analysis. The remainder of the pretreated bagasse samples were stored at 4 °C for enzymatic digestion. Compositional analysis of bagasse samples were conducted according to standard procedures developed by National Renewable Engergy Laboratory (NREL, US) (Sluiter et al., 2008). All reported compositional analyses were the means of duplicate samples.

2.2.2. Pilot scale pretreatment

Pilot scale pretreatments were conducted at the Mackay Renewable Biocommodities Pilot Plant, a Queensland University of Technology facility located on the side of the Racecourse Sugar Mill (Mackay, Australia). Pretreatments were conducted in a 150 L stainless steel horizontal reactor (Andritz, USA) (Fig. 1). Detailed information on the construction and layout of this reactor has been published previously (Wong et al., 2011). Glycerol was pumped into a solvent tank, where it was preheated to 100 °C, before being pumped to the pretreatment reactor. Sugarcane bagasse (20 kg, ~50 wt.% moisture) was mixed with ~8 kg of glycerol solution or water containing the required amount of acid. The mixed bagasse was delivered to the pretreatment reactor via conveyor. The horizontal reactor was preheated to the required pretreatment temperature prior to bagasse loading. After loading bagasse, ~42 kg glycerol or water was pumped into the reactor. An initial biomass loading (solid mass/liquid mass) of 17% was used in the pilot scale experiments. The initial water contents in liquid phase were ~17 wt.% for all the glycerol-associated pretreatments. The temperature of the reactor was maintained using saturated steam (14 bar, 195 °C). As a result, water was added into the reactions during pretreatment. Bagasse loading took between 10 and 15 min, with preheated glycerol delivery occurring within 2 min after loading was complete. Heating the reactor to the required pretreatment temperatures via addition of saturated steam took 3–5 min and pretreatment temperatures were maintained by the addition of steam. Mixing (20 rpm) was maintained from bagasse loading until the completion of pretreatment.

After pretreatment, the pretreated bagasses were immediately pressed to remove the hydrolysate and samples of the hydrolysate were collected for analysis. The reaction chamber was opened when the temperature of the reactor dropped below 90 °C. The samples (~200 g) were collected and washed with water (800 mL × 4). Portions of the washed samples were air-dried and milled for compositional analysis. The remainder of the washed samples were stored at 4 °C for enzymatic hydrolysis.

2.3. Enzymatic hydrolysis

Enzymatic hydrolyses of bagasse pretreated at the laboratory scale were carried out a 20 mL glass vials containing a 5.0 g mixture of pretreatment residue, buffer, and enzyme. Enzymatic hydrolyses of samples from pilot scale pretreatment were carried out in 250 mL flasks containing a 100 g mixture of pretreatment residue, buffer, and enzyme (since the samples with large fibre sizes were not suitable for enzymatic hydrolysis in a 20 mL glass vials). A glucan loading of 2 wt.% was used for all analyses. The reaction solutions contained 0.05 M citrate buffer to maintain