



# Facile, room-temperature pre-treatment of rice husks with tetrabutylphosphonium hydroxide: Enhanced enzymatic and acid hydrolysis yields



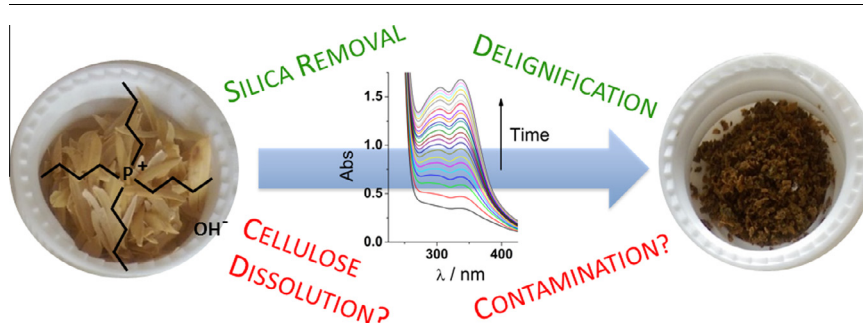
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## HIGHLIGHTS

- Tetrabutylphosphonium hydroxide (TBPH) can remove lignin and silica from rice husks.
- Mild pre-treatment facilitates enzymatic and acid hydrolysis glucose yields.
- Extensive pre-treatment enhances acid hydrolysis yield; reduces enzymatic yield.
- TBPH is incorporated in extensively disrupted biomass; inhibits cellulase enzymes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Aqueous solutions of tetrabutylphosphonium hydroxide have been evaluated as pretreatment media for rice husks, prior to sulphuric acid hydrolysis or cellulase enzymatic hydrolysis. Varying the water:tetrabutylphosphonium hydroxide ratio varied the rate of delignification, as well as silica, lignin and cellulose solubility. Pre-treatment with 60 wt% hydroxide dissolved the rice husk and the regenerated material was thus heavily disrupted. Sulphuric acid hydrolysis of 60 wt%-treated samples yielded the highest amount of glucose per gram of rice husk. Solutions with good lignin and silica solubility but only moderate to negligible cellulose solubility (10–40 wt% hydroxide) were equally effective as pre-treatment media for both acid and enzymatic hydrolysis. However, pre-treatment with 60 wt% hydroxide solutions was incompatible with downstream enzymatic hydrolysis. This was due to significant incorporation of phosphonium species in the regenerated biomass, which significantly inhibited the activity of the cellulase enzymes.

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## 1. Introduction

Lignocellulosic biomass refers to living or recently living material which is composed of primarily hemicellulose (hemicellulose and cellulose) and lignin (Alonso et al., 2010; Hossain and Aldous, 2012). Lignocellulosic biomass processing is becoming an

increasingly important aspect of green, sustainable chemistry, given its ability to potentially supplant polluting fossilised sources with renewable materials (Hossain and Aldous, 2012). Correspondingly, much attention has been devoted to the conversion of lignocellulosic biomass into liquid fuels (Alonso et al., 2010; Rinaldi and Schuth, 2009), hydrogen (Alonso et al., 2010; de Vrije et al., 2009), syngas (Alonso et al., 2010), value-added feedstocks (Hossain and Aldous, 2012), polymers (Zhao et al., 2008), silica (Foletto et al., 2006; Real et al., 1996; Sousa et al., 2009), silicon carbide (Foletto et al., 2006; Sharma et al., 1984), etc. Given the ingenious

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defensive structure that lignocellulosic biomass has developed over millions of years of evolution, chemistry often needs to be employed to break down the molecular superstructure before further processing can proceed (Alonso et al., 2010; Hossain and Aldous, 2012; Rinaldi and Schuth, 2009).

Wood is an abundant lignocellulosic biomass. However, the processing of waste from widely abundant, fast-growing agricultural products is more appropriate than deliberately harvesting wood. Rice husks are an agricultural crop waste which are obtained as a by-product of a rice milling process and are produced on a massive scale worldwide (Ludueña et al., 2011; Sousa et al., 2009; Zhao et al., 2008). In contrast to wood, rice husks already exist in small pieces hence no further mechanical treatment is necessary. Due to their widespread abundance and renewability, rice husks are ideal targets for further application. However, rice husks also possess a very high silica content (ca. 15–25 wt%) (Foletto et al., 2006; Ludueña et al., 2011; Real et al., 1996). Biomass sources with silica values above 0.5 wt% are known to cause significant wear, e.g. to the teeth of livestock when used as feed (Hummel et al., 2011) or to tools used in particle board production (Ludueña et al., 2011). When combined with the presence of lignin (ca. 20 wt%) it makes the husk extremely difficult to compost or to mechanically process the husks (Salanti et al., 2012). Instead they are frequently burnt (Foletto et al., 2006), with the residual silica sold or buried (Sousa et al., 2009; Zhao et al., 2008).

Previous treatment of rice husks with 'salty solvents' such as pure ionic liquids have required the application of high temperatures (exceeding 100 °C) (Ang et al., 2012; Lynam et al., 2012; Lynam and Coronella, 2014). Even then, only [Emim][acetate] (Ang et al., 2011, 2012; Lynam et al., 2012) (and recently [Emim][formate] plus glycerol (Lynam and Coronella, 2014)) have been noted to be effective, likely due to the basic carboxylate anions assisting in silica removal. Pretreatment of rice husks at 110 °C in [Emim][acetate] displayed the most complete lignin removal, the highest proportion of rice husk dissolution and the most vigorous surface disruption of the regenerated cellulose (Ang et al., 2011, 2012). It has been reported that the enzymatic hydrolysis of the generated cellulose after ionic liquid pretreatment resulted in higher reducing sugar yields than the untreated rice husks (Ang et al., 2012; Lynam et al., 2012). However, no recycling of the ionic liquid has been demonstrated, the role of silica is often neglected in such studies (Ang et al., 2012; Lynam et al., 2012), and high temperatures are required (Ang et al., 2012; Lynam et al., 2012; Lynam and Coronella, 2014). If such treatments could be conducted at room temperature using water this would represent a much more advantageous process (Brandt et al., 2011).

It has been established since at least the 1930s that tetraalkylammonium hydroxide solutions can dissolve cellulose at room temperature once the water content drops below a certain level, e.g. the hydroxide becomes only partially hydrated and can thus interact with and solubilise the cellulose (Strepikheev et al., 1957). However, this appears to have been somewhat overlooked in recent decades until Abe et al. (2012) demonstrated that 60 wt% solutions of tetrabutylphosphonium hydroxide (TBPH) in water can dissolve 20 wt% cellulose at room temperature (Abe et al., 2012). Ema et al. (2014) have since demonstrated that a 40 wt% solution of tetrabutylammonium hydroxide in water could also dissolve 10 wt% cellulose at room temperature, and Wei et al. (2015) have very recently demonstrated that lower temperatures (i.e. 16 °C) are far more favourable for cellulose dissolution than warmer temperatures (i.e. 28 °C).

Regarding lignocellulosic biomass, Hyväkkö et al. (2014) have demonstrated that TBPH cannot dissolve wheat straw (after 4 h), while Abe et al. (2014) demonstrated 60% of the polysaccharides could be dissolved from fine wood flour after 24 h stirring in

70 wt% TBPH at room temperature. If patient enough, grinding is not necessary as solid disks of wood could also be dissolved, albeit after a time period of months (Abe et al., 2014). Crucially, Hyväkkö et al. (2014) also outlined a method for the potential full recycle and recovery of the cationic component.

As opposed to ~100% ionic ionic liquids, a 20 wt% solution of TBPH in water is ~98 mol% water, representing a significantly 'greener' system. Additionally, the ability to effectively use partially hydrated hydroxides at room temperature represents a much lower energy consumption than ionic liquids which routinely need to be employed at temperatures exceeding 100 °C in order to dissolve biomass, and even then tend to be viscous (i.e. hard to stir). However, although demonstrated to be highly effective for cellulose dissolution (Abe et al., 2012; Ema et al., 2014), reports have indicated TBPH solutions are much slower and less effective at dealing with whole biomass (Abe et al., 2014; Hyväkkö et al., 2014).

Reported herein is the first investigation into the ability of partially hydrated TBPH solutions to disrupt and dissolve rice husks. Crucially, the heavy reliance of rice husks upon silica to form a robust shield can be actively exploited by using TBPH. TBPH can effectively remove silica and lignin within a few hours at room temperature. The solubility of common biomass components (lignin and silica) have been quantified in TBPH, and the effect of TBPH pre-treatment upon both acid hydrolysis and enzymatic hydrolysis yields has been evaluated for the first time. Room temperature pre-treatment of rice husks with TBPH dramatically improves the glucose yield, especially for acid hydrolysis.

## 2. Methods

All commercial reagents were purchased from Sigma–Aldrich (Castle Hill, Australia). All hazardous materials were kept from the environment and effectively handled following UNSW guidelines (document HS321), and following the plans and policies outlined in UNSW's Green Lab Environmental Compliance Program.

### 2.1. Scanning electron microscopy characterisation

The rice husk was mounted on a stainless steel stage via an adhesive carbon pad and sputter coated with chrome to provide a conductive surface. Subsequently it was analysed using a Nova NanoSEM 230 with a Bruker Silicon Drift Energy Dispersive X-ray microanalysis system. For high resolution images, the instrument was used in immersion mode, with a spot size of 2.5, and a working distance of approximately 5 mm. An initial elemental scan of the region was taken at a working distance of 6.6 mm and an accelerating voltage of 10 kV. This showed significant amounts of silicon, carbon and oxygen and small amounts of other elements. In the case of rice husk treated with high concentration of TBPH, significant amount of phosphorus was also found.

### 2.2. Characterisation of the chemical composition of the rice husks

#### 2.2.1. Water content

The water content of air-equilibrated rice husks (9.8 wt%) was determined by drying to a constant weight in a convection oven at 105 °C; all other values are reported against the dry weight of the rice husks.

#### 2.2.2. Extractives content

This was determined by extensively washing a known quantity of dried rice husks with dichloromethane in a Soxhlet extractor for 24 h (subsequent washing with acetone was found to have no effect). Dichloromethane was used solely in an analytical role,

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