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Research article

Transformation of oil palm fronds into pentose sugars using copper (II) sulfate pentahydrate with the assistance of chemical additive

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ABSTRACT

Among the chemical pretreatments available for pretreating biomass, the inorganic salt is considered to be a relatively new but simple reagent that offers comparable pentose (C5) sugar recoveries as the conventional dilute acid hydrolysis. This study investigated the effects of different concentrations (1.5–6.0% (v/v)) of H_2O_2 or $Na_2S_2O_8$ in facilitating $CuSO_4 \cdot 5H_2O$ pretreatment for improving pentose sugar recovery from oil palm fronds. The best result was observed when 0.2 mol/L of $CuSO_4 \cdot 5H_2O$ was integrated with 4.5% (v/v) of $Na_2S_2O_8$ to recover 8.2 and 0.9 g/L of monomeric xylose and arabinose, respectively in the liquid fraction. On the other hand, an addition of 1.5% (v/v) of H_2O_2 yielded approximately 74% lesser total pentose sugars as compared to using 4.5% (v/v) $Na_2S_2O_8$. By using $CuSO_4 \cdot 5H_2O$ alone (control), only 0.8 and 1.0 g/L xylose and arabinose, respectively could be achieved. The results mirrored the importance of using chemical additives together with the inorganic salt pretreatment of oil palm fronds. Thus, an addition of 4.5% (v/v) of $Na_2S_2O_8$ during $CuSO_4 \cdot 5H_2O$ pretreatment of oil palm fronds at 120 °C and 30 min was able to attain a total pentose sugar yield up to ~40%.

1. Introduction

Lignocellulosic biomass mainly exists in the form of agricultural wastes, energy crops, as well as forestry residues (Loow et al., 2015). Biomass is currently exploited as a renewable source of fermentable sugars, which are considered as one of the main building blocks for biofuels and specialty chemicals. It was estimated that 2×10^{11} tons of lignocellulosic biomass is produced globally every year, $8–20 \times 10^{11}$ tons of which is potentially accessible for processing (Choudhary et al., 2016). With the increasing of palm oil production which contributes to the national economy in Malaysia (Zahrim et al., 2015), palm biomass in gaining noteworthy attention and being increasingly utilized to produce various products such as bioethanol, vitamins, biofertilizer, and others. Up to 26.2 million tons of oil palm fronds (OPF) are produced annually in Malaysia, for each million ton of fresh fruit bunch processed (Yunus et al., 2010). In practice, OPF are usually left to degrade as mulch in the oil palm plantations after pruning process, to improve soil properties and water retention (Gandahi and Hanafi, 2014). However, this practice offers a limited value to the industry since OPF shows potential for sugar recovery with its chemical composition of 40–50%, 34–38%, and 20–21% of cellulose, hemicellulose, and lignin, respectively (Kotarska et al., 2015). Furthermore, sugar recovery from OPF would provide an environmentally friendly alternative in biomass handling, instead of degrading OPF on the open land. Thus, OPF has the potential to serve as a sustainable carbon source in biorefineries (Tan et al., 2016).

The complete transformation of lignocellulosic biomass into value-added products can be divided into two stages, namely biomass pretreatment and thermochemical or biological processing of biomass (Loow et al., 2016b). Biomass pretreatment is an essential step in biomass transformation because cellulose, hemicellulose, and lignin form a complex biomass structure that is highly resistant to hydrolysis and microbial digestion (Achinas and Euverink, 2016). Lignin, in particular, is a phenolic macromolecule which acts as the main physical barrier in the recalcitrance of biomass (Loow et al., 2016a). As such, Mosier et al. (2005) necessitate the hydrolysis of the lignin structure during a pretreatment process, in order to render the biomass more suitable for downstream fermentation. Recently, the use of inorganic salts such as KCl, NaCl, $CaCl_2$, $MgCl_2$, $CuCl_2$, $FeCl_3$, and $AlCl_3$ has been explored as one of the alternative ways of pretreating biomass (Linares et al., 2013; Liu et al., 2009a,b; Lu and Zhou, 2011; Monavari et al., 2011; Park et al., 2010), as compared to the conventional systems

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such as dilute acid and alkali pretreatment (Loow et al., 2016a). Inorganic salt provides several advantages over the traditional dilute acid hydrolysis, namely lesser corrosiveness for certain salts (Chen et al., 2014) as well as the possibility of recycle and reuse of salt during pretreatment (Kamireddy et al., 2013). Among all the inorganic salts studied, $CuSO_4$ remains as one of the least explored. Hence, in this study, the performance of copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) would be tested for sugar conversion from OPF. Leipner et al. (2000) reported that inorganic hydrate salts such as $ZnCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were able to cause cellulose dissolution. Furthermore, the relatively low cost of many hydrated metal salts coupled with their air/moisture insensitivity makes their use in large scale industrial processes viable (Smith et al., 2014).

One of the bottlenecks for most inorganic salt pretreatments, like dilute acid hydrolysis, is the need to operate at high temperatures (150–200 °C) in order to achieve significant hydrolysis of hemicellulose. Previously, Diaz et al. (2014) reported an improvement of sugar recovery up to 75% when hydrogen peroxide (H_2O_2) was added to alkaline pretreatment of rice husk. The rate of enzymatic hydrolysis was also accelerated by optimizing the concentration ratio of H_2O_2 and transition metal ions Fe^{2+} under room temperature (Kato et al., 2014). Another oxidizing agent worth investigating is sodium persulfate ($Na_2S_2O_8$), which is commonly used for surfactant removal or groundwater remediation (Furman et al., 2010; Rastogi et al., 2009). Sulfate radicals ($SO_4^{-}\bullet$) which are generated by $Na_2S_2O_8$ have been reported to be stronger and more selective oxidants than the hydroxyl radicals ($OH\bullet$) which are produced from H_2O_2. Interestingly, transition metal ions were useful in aiding the efficient generation of radicals from $H_2O_2/Na_2S_2O_8$ (Liu et al., 2012; Simpson et al., 1988). To the best of our knowledge, there have been little to no studies regarding the use of an inorganic salt coupled with an oxidizing agent for biomass pretreatment purpose. It was postulated that H_2O_2 and $Na_2S_2O_8$ were able to aid $CuSO_4 \cdot 5H_2O$ hydrolysis of OPF during inorganic salt pretreatment. Thus, the main objective of this study was to recover pentose sugars (xylose and arabinose) from OPF using $CuSO_4 \cdot 5H_2O$ pretreatment at 120 °C and 30 min, and also to evaluate the effects of H_2O_2 and $Na_2S_2O_8$ additives in enhancing sugar recovery during the pretreatment process.

2. Materials and methods

2.1. Biomass feedstock and chemicals preparation

Fresh OPF were obtained from an oil palm plantation, owned by Universiti Kebangsaan Malaysia and their leaflets were removed. A sugarcane press machine was used to extract the solid petioles residue, after that the petioles were sun-dried for two days. Next, these residues were ground in a pulverizer set at 6000–7000 rpm, in which the particles of size ≤0.5 mm were collected after passing through a mechanical sieve. After that, the OPF were dried at 55 °C for 48 h in an oven to remove any remaining moisture, and stored in a container with a tight-fitting lid filled with desiccants at room temperature until further use. High-grade monomeric sugars (99%) (D (+) glucose, D (−) xylose, and L (+) arabinose) were used for calibration of standard curves, while the $CuSO_4 \cdot 5H_2O$, H_2O_2, $Na_2S_2O_8$, as well as other chemicals used in this study were ensured to be analytical grades.

2.2. Chemical composition of OPF

The chemical composition of OPF was determined by adapting the standard laboratory analytical procedure (LAP) from the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2008). Soxhlet extraction was performed using 200 mL of distilled water to determine the number of water extractives, in which the water extracted samples further underwent 200 mL of ethanol extraction to determine the number of ethanol extractives. On the other hand, OPF samples in porcelain crucibles were burned in a furnace at 575 °C for 24 h (Sluiter et al., 2008), in which the ash content was then determined by the weight of the remaining solids after undergoing calcination. The cellulose, hemicellulose, and lignin contents were also determined using the acid hydrolysis method described in the NREL LAP protocol.

2.3. $CuSO_4 \cdot 5H_2O$ pretreatment with/without H_2O_2 or $Na_2S_2O_8$ additives

Firstly, 2.5 g of OPF samples were transferred into 50 mL Schott bottles. The $CuSO_4 \cdot 5H_2O$ aqueous solutions were prepared at a range of 0.2–0.8 mol/L concentrations. The inorganic salt solutions were then transferred into the Schott bottles containing OPF samples at a fixed solid-to-liquid ratio of 1:10 (w/v). Next, the mixtures were sent for reaction at 120 °C and 30 min. After the completion of the reaction, the mixtures were then removed at a cooling temperature of approximately 75 °C and air cooled to quench the reaction. A small portion of the pretreatment hydrolysate was extracted and centrifuged at a speed of 13,500 rpm for 10 min using a Mini 1312M Micro Centrifuge, before passing through a 0.22 μm syringe filter for sugar content analysis. On the other hand, the pretreated OPF solids were washed with distilled water to remove any residue of pretreatment solvent, dried overnight in an oven at 55 °C, and stored in a container with desiccants before undergoing further characterization studies. To study the effects of oxidizing agents, the same procedure was repeated but with an addition of H_2O_2 or $Na_2S_2O_8$ at varying concentrations (1.5–6.0% (v/v)) to the $CuSO_4 \cdot 5H_2O$ solution before the reaction at 120 °C and 30 min. Fig. 1 shows a general flow diagram of the $CuSO_4 \cdot 5H_2O$ pretreatment of OPF with or without the assistance of H_2O_2 or $Na_2S_2O_8$.

2.4. Analytical methods

2.4.1. Analysis of sugar content in hydrolysate using high performance liquid chromatography (HPLC)

The yield of monomeric sugars (glucose, xylose, arabinose) was analyzed using an Agilent series 1200 Infinity HPLC system equipped with Refractive Index (RI) detector and a Bio-Rad Aminex HPX-87H column. The column was operated at a flow rate of 0.4 mL/min with 0.005 mol/L H_2SO_4 as the mobile phase. The temperature of the column was set at 65 °C, while the RI detector was set at 40 °C to minimize the effects of the temperature gradient. The concentration of the sugars was analyzed in g/L by comparing the chromatogram with the concentration of known sugar standards. Lastly, the % recovery of monomeric sugars was calculated using the formula adapted from Kamireddy et al. (2013):

$$\%\ \text{recovery of sugar} = \frac{\text{sugar recovered}(\text{g/L})\,\text{volume of solvent used}(\text{L})}{\text{OPF carbohydrate composition}(\%)\,\text{mass of OPF used in pretreatment}(\text{g})} \times 100\%$$