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Improvement of xylose recovery from the stalks of oil palm fronds using inorganic salt and oxidative agent

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ABSTRACT

Lignocellulosic biomass is a plant dry matter that could be considered as a renewable carbon resource for the production of reducing sugar, which is an alternative building block for biofuels and chemicals. However, due to the recalcitrant nature of lignocellulosic biomass, researchers have focused their efforts on establishing cost-efficient pretreatments to reutilize the lignocellulose components within the biomass effectively. In this study, divalent ($CuCl_2$) and trivalent ($FeCl_3$) inorganic salts were used in the recovery of xylose from the stalks of oil palm fronds (OPF). Additionally, oxidizing agents such as hydrogen peroxide and sodium persulfate were tested for their effectiveness in improving inorganic salt pretreatment. By using inorganic salt alone, $FeCl_3$ outperformed $CuCl_2$ in terms of xylose recovery, in which 75.5 and 59.3% of xylose could be recovered from OPF using $FeCl_3$ and $CuCl_2$, respectively. An incorporation of sodium persulfate with $CuCl_2$ enabled a maximum xylose recovery up to 72.0%, with no statistical difference as compared to using $FeCl_3$ alone. The synergism between $CuCl_2$ and sodium persulfate was attributed to the formation of unstable Cu^{3+} ions, which acted as a trivalent salt. Characterization studies of the solid fraction before and after pretreatment also validated the delignification of OPF. Hence, the combination of $CuCl_2$ and sodium persulfate was able to attain sugar yields which were comparable with other conventional pretreatments.

1. Introduction

Currently, lignocellulosic biomass is generated significantly as a by-product on a global scale, with a projected production rate of 680 million tons annually by 2030 in the United States alone [1]. Until now, researchers are still continuously searching methods to reutilize lignocellulosic biomass. For example, agricultural residues such as rice husks have been scrutinized for producing silica and generating electricity via gasification [2], as well as undergoing biodegradation to form biofertilizers [3]. At present, Malaysia is one of the largest exporters of crude palm oil in the world [4]. Also, the Malaysian oil palm industry has been recognized as one of the largest contributors of lignocellulosic biomass, with more than 90% of the country's total biomass deriving from 5.4 million hectares of oil palms [5]. Among the oil palm wastes, oil palm fronds are the most abundant solid wastes generated by the oil palm industry in most Asian and African countries [6]. Approximately 26.2 million tons/y of oil palm fronds are produced per million of fresh fruit bunch processed. The production of oil palm fronds outweighs the production of other oil palm by-products, such as oil palm trunks (7.0 million tons/y) and empty fruit bunches (0.23 million tons/y) [7]. In practice, oil palm fronds are left to rot in the plantations, as it is believed that the degradation can improve soil qualities [8]. However, this practice offers limited value to the industry. In addition, the improper stacking of oil palm by-products on land may become the breeding site of pests such as rhinoceros beetles and rats [9]. On the contrary, there is a huge prospect of recovering sugar from oil palm fronds because oil palm fronds consist of 40–50, 34–38, and 20–21% of cellulose, hemicellulose, and lignin, respectively [10]. Hence, utilizing this biomass for sugar conversion may reduce existing biomass disposal issues and improve the sustainability of oil palm industry. The bioprocessing of lignocellulosic biomass is granted further economic value, since it is a potential solution to the current issues of depleting fossil fuel reserves and the air pollution problems associated with its use [11].

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The complex recalcitrant structure of the biomass prevents it from being efficiently hydrolyzed or digested by the microorganisms during fermentation process [12]. Hence, a pretreatment stage is usually essential to overcome the biomass recalcitrance for having effective biomass utilization [13]. Several pretreatment approaches have been explored, such as physical (milling, energy irradiation), physicochemical (liquid hot water, steam explosion), chemical (acid, alkali, organosolv), and biological pretreatments (bacteria mediation) [14,15]. Inorganic salt is regarded as one of the newer methods of pretreatment that has been recently proven to demonstrate favorable sugar recoveries [16]. From the direct use of inorganic salts to their integration with other methods in pretreating biomass, inorganic salts such as KCl, NaCl, $CaCl_2$, $MgCl_2$, $FeCl_3$, $CuCl_2$, $FeSO_4$, and $AlCl_3$ have been proven to effectively increase the hydrolysis rate and sugar yields of cellulose and hemicellulose [17–21]. The utilization of inorganic salts brings about several advantages over the conventional dilute acid pretreatment, particularly from an economic standpoint. For example, certain inorganic salts are less corrosive in nature as compared to acids [22], since the former undergoes hydrolysis to form weaker electrolytes for a steadier reactive environment [23]. Thus, the construction of equipment using expensive materials could be avoided. Although the use of inorganic salts for pretreating biomass raises some environmental concerns, certain inorganic salts could be recovered using ultrafiltration, and subsequently recycled and reused throughout the pretreatment process [24]. However, to achieve greater removal of hemicellulose, most inorganic salt pretreatments require high temperatures, typically ranging between 150 and 200 °C [17–29].

Hydrogen peroxide (H_2O_2) is known as an enhancer to improve wastewater treatment efficiency [30], but lately, H_2O_2 is also attempted in assisting biomass processing. According to Zheng et al. [31], H_2O_2 treatment is a non-selective oxidation process which has the capability to break down lignin and hemicellulose to a certain extent via the action of hydroxyl radicals ($HO^{\cdot}$). Diaz et al. [32] showed that the addition of H_2O_2 during alkaline pretreatment of rice husk improved the overall sugar recovery by 75%. In addition, no by-product formation was found in the biomass hydrolysate from the synergized pretreatment of alkali-H_2O_2 [33]. Also, Ofori-Boateng and Lee [34] found that sono-assisted organosolv/H_2O_2 pretreatment of OPF improved the yield of bioethanol using same vessel saccharification and fermentation. On the other hand, sodium persulfate ($Na_2S_2O_8$) is commonly used as a source of sulfate radical ($SO_4^{-\cdot}$) during In Situ Chemical Oxidation, because the $SO_4^{-\cdot}$ acts as a strong oxidant for removing surfactant or improving groundwater remediation [35,36]. Through different mechanisms such as the removal of hydrogen atom from a saturated carbon chain or by removing electrons from a carboxylate compound, $SO_4^{-\cdot}$ was able to degrade a wide variety of organic compounds at relatively shorter treatment durations [37]. Furthermore, $SO_4^{-\cdot}$ was known to remove hydrogen from the hydroxyl groups in the hemicellulose backbones that were present in semi-interpenetrating polymeric networks hydrogels [38]. Hence, H_2O_2 and $Na_2S_2O_8$ might be able to aid inorganic salt hydrolysis of lignocellulosic biomass.

To the best of our knowledge, no investigation has been carried out to determine the synergistic effect of inorganic salt and oxidizing agents in the pretreatment of biomass. It was hypothesized that oxidizing agent produced free radicals which disrupted the lignin structure and thus could help facilitate inorganic salts in hydrolyzing the hemicellulose from the biomass. Therefore, the objective of this work was to evaluate the use of divalent ($CuCl_2$) or trivalent ($FeCl_3$) inorganic salts in the pretreatment of oil palm fronds stalks. In addition, the effect of inorganic salt plus oxidizing agent (H_2O_2 or $Na_2S_2O_8$) would also be investigated.

2. Materials and methods

2.1. Preparation of lignocellulosic biomass feedstock and chemicals

Fresh oil palm fronds were obtained from an oil palm plantation owned by Universiti Kebangsaan Malaysia and its leaflets were removed. A sugarcane press machine was used to remove the liquid from the stalks of oil palm fronds, and the pressed stalks were sun-dried for two days. The dry stalks were then collected and cut into smaller pieces so that they could be ground in a pulverizer (8000 rpm). After that, the ground stalks of oil palm fronds passed through a mechanical sieve so that only $\leqslant$0.5 mm particles were used in this study. The stalks of oil palm fronds particles with $\leqslant$0.5 mm in size were termed as OPF throughout this study. Next, the OPF were dried at 55 °C for 48 h in an oven. The OPF particles were then stored in a container with a tight-fitting lid filled with desiccants, under dry conditions at room temperature until further use. High-grade monomeric sugars (99%) (D (+) glucose, D (−) xylose, L (+) arabinose) and inhibitors (5-hydroxymethyl furfural, furfural, acetic acid) were used for calibration of standard curves. $CuCl_2$, $FeCl_3$, H_2O_2, $Na_2S_2O_8$, and other chemicals used in this study were ensured to be of analytical grades.

2.2. OPF compositional analysis

Compositional analysis of OPF was carried out by adapting the standard laboratory analytical procedure from National Renewable Energy Laboratory [39]. For water and ethanol extractives, the analysis was performed using a two-step Soxhlet extraction under reflux system. Water extraction (8 h) was done using 200 mL of distilled water, and the water extracted sample was followed by another Soxhlet extraction (24 h) using 200 mL of 95% ethanol to remove chlorophyll, waxes and other minor components [40]. For ash content analysis, the samples of OPF in porcelain crucibles were placed in a furnace at 575 °C for 24 h. After heating, the crucibles were removed from the furnace and kept in a desiccator. The samples were allowed to cool down for 1 h before weighing the ash. On the other hand, the cellulose, hemicellulose, and lignin compositions were determined using acid hydrolysis method [39]. After undergoing vacuum filtration, the filtrate was centrifuged (13,500 rpm for 10 min). The supernatant was filtered through 0.22 μm syringe filter and the filtered sample was sent for HPLC analysis to determine the sugar contents. The lignin content was determined using the dry weight difference of the filter paper before and after vacuum filtration [39].

2.3. H_2O_2/$Na_2S_2O_8$-assisted pretreatment using inorganic salt solution

Firstly, 2.5 g of OPF samples were transferred into 50 mL Schott bottles. The inorganic salt solutions ($CuCl_2$/$FeCl_3$) were prepared at a range of 0.1–0.8 mol/L concentration. The salt solutions were then transferred into the Schott bottles containing OPF samples at a fixed solid-to-liquid ratio of 1:10 (w/v). Oxidizing agents (H_2O_2/$Na_2S_2O_8$) were then added thoroughly into the mixture at different concentrations (1.5–6.0% (v/v)). The mixtures were then subjected to a reaction at a fixed temperature of 120 °C and duration of 30 min. The Schott bottles were removed (~70 °C) and air cooled, so that the reaction was quenched. After the pretreatment solution was cooled down, a small portion of the liquid fraction was extracted and centrifuged at a speed of 13,500 rpm for 10 min using a Mini 1312M Micro Centrifuge. The centrifuged hydrolysate was then transferred into a vial by passing through a 0.22 μm syringe filter for determining monomeric sugars (glucose, xylose, arabinose) and inhibitors (5-hydroxymethyl furfural, furfural, acetic acid) contents.