Pretreatment of oil palm frond using hot compressed water: An evaluation of compositional changes and pulp digestibility using severity factors

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ABSTRACT

The influence of reaction temperature (160–200 °C), residence time (45–90 min), and liquid–solid ratio (8–16 v/w) on oil palm frond (OPF) pre-treated with hot compressed water (HCW) was evaluated using severity factors. Effect of the process parameters studied on pulps composition and digestibility were found to be complex. The results revealed that digestibility could not be predicted merely according to composition. Severity factor was correlated with compositional changes and digestibility with good R-squared values at varied liquid–solid ratios (8–16 v/w), but not with overall glucose yield. HCW pretreatment significantly improved the overall glucose yield up to 83.72% with severity of 3.31 and liquid–solid ratio of 8.0 compared to untreated raw OPF which only recorded an overall glucose yield of 30.97%. HCW is therefore an effective method for pretreatment of OPF for glucose recovery.

1. Introduction

Lignocellulosic biomass intended for the production of second generation bioethanol requires pretreatment to allow the release of fermentable sugars from the plant polymers. Hydrothermal pretreatment was found to effectively improve the digestibility of lignocellulosic biomass (Knezevic et al., 2009; Yu et al., 2008). Hot compressed water (HCW) is a suitable medium for hydrolysis and hydrothermal process. Water around 200 °C in liquid form can be considered as HCW (Kruse and Dinjus, 2007). Similar to steam pretreatment, the objective of the HCW is to solubilize mainly the hemicellulose fraction as liquid–soluble oligosaccharides. The properties of water are changed at elevated temperature and pressure, especially when near the critical point where water changes its character as a solvent for ionic species to a solvent for non-ionic species as a high content of hydronium ions causes the pH to drop to around 4 (Brunner, 2009). The relatively low pH is suitable for acid-catalyzed reactions. Furthermore, the solubility of organic compounds in HCW increases compared to that in water at ambient condition. By using HCW, it is possible to break the strong cellulose–hemicellulose–lignin associations to increase the accessibility of enzymes to cellulose. Generally, the reactions of HCW are categorized as "hydrolysis reactions". HCW also alters the structure of cellulose and enables accelerated enzymatic hydrolysis as the cellulose decrystallizes into an amorphous form.

In terms of pretreatment quality, pulp digestibility and overall recovery of glucose from the biomass are the important goals. Three major parameters effect the successful outcome of pretreatments: reaction temperature, residence time and liquid–solid ratio. The biomass is often contacted with water at temperatures from 170–230 °C and at pressures of 25–100 bar (Schacht et al., 2008). In general, particle size reduction is not required for this pretreatment (Mosier and Wyman, 2005). In order to protect the sugars in their oligomeric form, moderate temperatures (<260 °C) should be applied (Schacht et al., 2008). HCW pretreatment generates a higher amount of solubilized products, but at lower concentrations than steam pretreatment (Bobleter, 1994; Hendriks and Zeeman, 2009) due to high water input. These low concentrations reduce the generation of degradation products like furfural and the condensation and precipitation of lignin compounds (Hendriks and Zeeman, 2009). Pressure has little influence and usually is adjusted to slightly higher than the vapor pressure of water to keep the medium in liquid form. Since it is not easy to evaluate these factors under different conditions, the concept of "severity factor" was introduced and it provides a way to compare the combined effects of parameters on the changes in pulps composition to enable a better comparison of results and a better correlation with the compositional changes in the biomass after pretreatment (Overend and Chornet, 1994).

Therefore, the objective of this work is to study the effect of reaction temperature, residence time and liquid–solid ratio on HCW pretreatment of oil palm frond (OPF) in a batch system and using the severity factor to investigate composition changes,

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digestibility and overall glucose yield. The effect of composition changes on digestibility is discussed.

2. Methods

2.1. Materials

OPF was collected from oil palm cultivation in the Engineering Campus of Universiti Sains Malaysia, Penang, Malaysia. The material was shredded and ground using a blender to a particle size smaller than 1 mm by passing through 1-mm sieve screens using a vibrator sieve shaker (Retsch, Germany). The particles were dried under the sun with an average temperature of 32 °C for 3 days to a final moisture content of 10.26%. The flat plate-shaped particles were present in the following size distribution: 0.500–1.000 mm (58.68 wt%), 0.250–0.500 mm (15.72 wt%), 0.125–0.250 mm (2.98 wt%) and <0.125 mm (22.63 wt%).

Enzymes used for hydrolysis were Novozyme 188 (263 CBU/g) and Celluclast 1.5 L (798 EGU/g) (Novozyme, Denmark) obtained from Science Technics Sdn Bhd. One cellobiase unit (CBU) is the amount of enzyme that degrades cellobiose to 1 µmol glucose per minute at 40 °C and pH 5.0. One endo-glucanase unit (EGU) is defined as the amount of enzyme required to halve the viscosity of a solution of carboxymethylcellulose under standard conditions (pH 6.0, 40 °C, 30 min. incubation).

2.2. Characterization

2.2.1. Determination of extractives

Determination of extractives in OPF was carried out according to the Laboratory Analytical Procedure for Determination of Extractives in Biomass (Ehrman, 1994). Samples were washed with deionized water and dried overnight at 80 °C prior to analysis. The analysis was carried out by a two-step Soxhlet extraction. First, hot water extraction (under reflux) was carried out for 8 h to remove water-soluble compounds such as inorganic material, non-structural sugars and nitrogenous material. The sample was weighed to the nearest 0.1 mg and added to the extraction thimble for extraction in a Soxhlet apparatus containing 200 mL of deionized water. Upon completion, the sample was carefully removed from the thimble and dried. This was followed by another Soxhlet extraction with 200 mL of 95% ethanol for 24 h to remove chlorophyll, waxes and other minor components. Triplicate samples were used and average values were calculated. The percentage of extractives was calculated using the following equation:

$$\% \text{ Extractives} = \frac{\text{Weight}_{\text{thimble+sample (before)}} - \text{Weight}_{\text{thimble+sample (after)}}}{\text{Weight}_{\text{sample}}} \times 100\%$$

(1)

2.2.2. Determination of chemical composition

OPF (2.5 g) was heated with 150 mL of water at 75 °C, 0.2 mL acetic acid and 2.0 g $NaClO_2$ were added into the slurry, and after 1, 2 and 3 h, 0.2 mL acetic acid and 1.0 g $NaClO_2$ were added. The slurry was filtered through gravity filtration and washed with distilled water and acetone. The delignified residue (holocellulose) was weighed after drying for 24 h in an oven at 105 °C (Teramoto et al., 2009). The α-cellulose content was determined as the amount of residue insoluble in a 17.5% NaOH aqueous solution according to TAPPI 203: 1 g of holocellulose was transferred into a flask with 25 mL of 17.5% aqueous NaOH solution and stirred for 40 min at 20 °C and subsequently filtered through gravity filtration. Washing and filtration were carried out using 40 mL of a 10%

acetic acid aqueous solution and 1 L of boiling water at two different stages. The remaining wet solid (α-cellulose) was dried in an oven (105 °C) and weighed. Hemicellulose content was determined by subtracting the α-cellulose content from the holocellulose content (Teramoto et al., 2009). Triplicate untreated samples and duplicate pretreated samples were used, and average values were calculated. The quantity of hemicellulose and cellulose were determined using the following equation:

$$\% \, \alpha - \text{Cellulose} = \frac{\text{Weight}_{\text{cellulose}}}{1 \text{ g}} \times \frac{\text{Weight}_{\text{holocellulose}}}{\text{Weight}_{\text{sample}}} \times 100\%$$

(2)

$$\% \, \text{Hemicellulose} = \frac{\text{Weight}_{\text{holocellulose}}}{\text{Weight}_{\text{sample}}} \times 100\% - \%\alpha - \text{Cellulose}$$

(3)

To investigate Klason lignin content, the samples were hydrolyzed with 72% sulfuric acid for 1 h at 30 °C, with a ratio of 0.15 g dry mass to 5 mL of 72% sulfuric acid. The mixture was diluted to 3% sulfuric acid by adding water up to 45 mL of total volume and autoclaved. The mixture was vacuum filtered using filter crucibles. The dried residues obtained were weighed to give the Klason lignin content.

$$\% \, \text{Klason lignin} = \frac{\text{Weight}_{\text{dried residues}}}{0.15 \text{ g}} \times 100\%$$

(4)

2.2.3. Determination of ash content

Ash content in OPF was determined based on the Laboratory Analytical Procedure for Determination of Ash in Biomass provided by NREL (Sluiter et al., 2005). In the procedure, triplicate samples of biomass in porcelain crucibles were placed in a muffle furnace (Carbolite RWF1200, England) at 575 °C for 12 h. After the heating process, the crucibles were removed from the furnace and cooled down to room temperature for 4 h before weighing the crucibles and ash to the nearest 0.1 mg. Subsequently, the crucibles and ash were placed in the furnace again for another 4 h and then cooled down to room temperature for weighing. The procedures were repeated until constant weight of samples was obtained. Ash content was then calculated based on the following equation:

$$\% \, \text{Ash} = \frac{\text{Weight}_{\text{crusible+ash}} - \text{Weight}_{\text{crusible}}}{\text{Weight}_{\text{sample}}} \times 100\%$$

(5)

2.3. Hot compressed water pretreatment

HCW pretreatment was carried out using a batch reactor with a programmed temperature controller. The stainless-steel reactor has a volume capacity of 500 mL, designed to a maximum temperature of 200 °C and pressure of 30 MPa with a manometer pressure gauge mounted on the head fitted using a Swagelok fitting. This gauge was used to measure the internal pressure of the reactor. The reactor is also equipped with an electric heater with an insulation-cased with a stainless steel jacket, a thermocouple immersed in the liquid mixture and magnetic stirrer. The heating rate was approximately 5 °C/min. N_2 gas was used for purging and pressurizing the vessel. Initially, dried OPF was charged into the reactor. Deionized water was added to the desired liquid–solid ratio (v/w). The reactor was kept sealed and pressurized to 10 bar to keep the water in liquid form. The reactor temperature was controlled with a programmable PID temperature controller. Once the mixture temperature reached the selected value, the magnetic stirrer was switched on at maximum speed to avoid mass transfer limitations. After the designed reaction time, the reactor was quickly cooled with ice to a temperature lower than 100 °C and slowly depressurized. The liquid and solid fractions were separated through filtration.