Optimization of dilute acid-catalyzed hydrolysis of oil palm empty fruit bunch for high yield production of xylose

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ABSTRACT

Cost-effective hydrolysis of lignocellulose at low acid concentrations to get high yield of sugars is commercially attractive but challenging. Oil palm empty fruit bunch (EFB) was hydrolyzed to get fermentable sugars using sulfuric acid and/or phosphoric acid whose concentrations were maintained at <1% (w/v) to favor their direct use in the subsequent fermentation processes as essential nutrient elements (S and P). Two types of kinetic models were used to describe the hydrolysis process and the Biphasic model was found to better predict the experimental results than the Saeman model and thereby used to guide the optimization of the hydrolysis process. It predicts that 80–90% xylose yield is achieved when EFB hydrolysis is conducted at 140–160 °C, liquid to solid ratios of 10–20 ml/g, 0.25–0.5% (w/v) of sulfuric acid and 0.1–0.2% (w/v) of phosphoric acid. The maximal xylose yield of 91.3% was experimentally obtained for EFB hydrolysis catalyzed by 0.5% (w/v) of H_2SO_4 and 0.2% (w/v) of H_3PO_4 at 160 °C, a liquid to solid ratio of 20 ml/g for 10 min, which is in well agreement with the model prediction and is comparable with the reported maximal xylose yields of 80–90% at higher acid concentrations (>1%, w/v). The combined use of H_2SO_4 and H_3PO_4 has a synergistic effect in improving xylose yield compared to using H_2SO_4 alone. An EFB particle diameter of 2 mm is optimal for getting the highest xylose yield.

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1. Introduction

Lignocellulose is the most abundant renewable resource on earth, and conversion of this low cost biomass to fuels and chemicals has received much attention [1,2]. Pretreatment of lignocellulose to get fermentable sugars is an essential step for lignocellulose conversion by microbial fermentation. A variety of pretreatment methods utilizing mechanical, chemical and biological processing have been developed for altering the structural and chemical compositions of lignocellulose to improve the sugar yield. Among them, dilute acid-catalyzed hydrolysis has been most frequently investigated due to its promising commercial feasibility [1].

Oil palm empty fruit bunch (EFB) is a lignocellulosic waste produced during palm oil extraction with an estimated worldwide production of ca 12 million tons (dry weight) per year [3,4]. EFB is usually burned in incinerators of palm oil mills causing environmental pollution [5–7]. EFB is composed of cellulose (30–40%),

hemicellulose (20–30%) and lignin (20–30%) with xylan being the major component of hemicellulose. EFB can be hydrolyzed to sugars as valuable carbon sources for production of a variety of chemicals either chemically or biologically [5,8]. Xylan is very susceptible to hydrolysis by mild acid treatment due to the amorphous structure of hemicellulose compared to the highly crystallized cellulose [1]. Dilute acid-catalyzed hydrolysis of lignocellulose has been extensively studied for sugarcane bagasse and corn stover [9–15] with only a few reports for EFB [5].

Sulfuric acid and phosphoric acid are cheap and efficient acids for hydrolysis of lignocellulose. They also contain the essential elements S and P for microbial growth. After hydrolysis and neutralization, these acid components could be directly utilized as nutrient elements for microbial fermentation if their concentrations are kept at the levels of 0.5–1% (w/v) as required by most microbial fermentation processes [16–20]. However, majority of researchers usually utilized high acid concentrations (1–3%, w/v) [5,9–15] from the viewpoint of hydrolysis efficiency only without considering the required levels of the acid components by the subsequent fermentation processes. Acid concentration is an important factor affecting sugar release. Optimal xylose yields of 80–90% could be obtained at acid concentrations higher than 1% (w/v) [5,9–15]. When acid concentration was below 1% (w/v), xylose yield dropped significantly [12,21,22]. Therefore, it is a challenge to obtain

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high sugar yield at low acid concentrations for lignocellulose hydrolysis [23].

In this work, we focused on EFB hydrolysis catalyzed by dilute sulfuric acid and phosphoric acid whose concentrations were maintained at <1% (w/v) to favor their direct use in subsequent fermentation processes as essential nutrient elements (S and P). The hydrolytic process was simulated by kinetic models to guide the process optimization.

2. Materials and methods

2.1. Raw materials

EFB (moisture content 7%, w/w) was kindly provided by Wilmar International Limited, Singapore. It was sun-dried and grinded to small particles by a knife mill with 1 mm screen (unless otherwise specified), followed by oven-drying at 80 °C for overnight before use. EFB compositions were analyzed following the standard procedures of NREL [14]. For getting EFB particles of different sizes, 2 mm, 4 mm and 8 mm screens were also used, respectively.
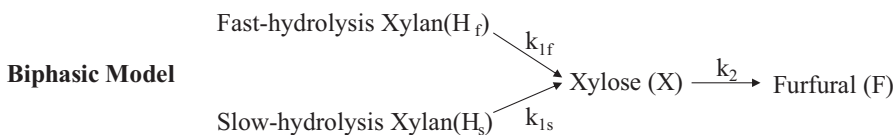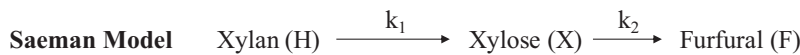
2.2. Acid hydrolysis

Acid-catalyzed hydrolysis of EFB was carried out in 1 L Parr reactors (Fike, Blue Springs, MO, USA). EFB (15–50 g) was added into 300 ml water containing 0.25–0.5% (w/v) of H_2SO_4 or 0–0.4% (w/v) of H_3PO_4 or both. The temperature was raised to predetermined levels (140–160 °C) for hydrolysis. After reaching the required reaction time, the reaction mixture was immediately cooled down to room temperature by circulated cooling water. The solid was separated from liquid by filtration and the filtrate was analyzed by HPLC.

2.3. Analytical methods

Xylose, glucose, arabinose and acetic acid were analyzed by HPLC (LC-10AT, refractive index detector SPD-10A, Shimadzu, Kyoto, Japan) with a Bio-Rad Aminex HPX-87 H column (Bio-Rad, Hercules, CA, USA) at 30 °C. The mobile phase was 5 mM H_2SO_4 at 0.6 ml/min.

2.4. Mathematic description of kinetic models

The Saeman model and Bipahsic model have been widely accepted to describe the kinetics of xylan hydrolysis [12,24]:

slow hydrolysis fractions differ only slightly per substrate and typically account for about 65% and 35%, respectively [24]. The kinetic models suggest that acid concentration, temperature and reaction time be synergistically adjusted to favor xylose accumulation by minimizing sugar degradation [12,24].

The two kinetic models are mathematically described as below [12,24].

Saeman model:

$$\frac{d[H]}{dt} = -k_1[H] \tag{1}$$

$$\frac{d[H]}{dt} = -k_1[H] - k_2[X] \tag{2}$$

$$\frac{d[F]}{dt} = -k_2[X] \tag{3}$$

$$[X] = \frac{k_1[H_0]}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{4}$$

where $[H]$, $[X]$ and $[F]$ represent the concentrations of xylan, xylose and furfural, respectively ($[X_0] = 0$, $[F_0] = 0$); k_1 and k_2 are the rate constants of xylan hydrolysis and xylose degradation, respectively.

Biphasic model:

$$\frac{d[H_f]}{dt} = -k_1[H_f] \tag{5}$$

$$\frac{d[H_s]}{dt} = -k_{1s}[H_s] \tag{6}$$

$$\frac{d[X]}{dt} = -k_{1f}[H_f] - k_{1s}[H_s] - k_2[X] \tag{7}$$

$$\frac{d[F]}{dt} = k_2[X] \tag{8}$$

$$[X] = \frac{k_{1f}[H_f]_0}{k_2 - k_{1f}}[\exp(-k_{1f} t) - \exp(-k_2 t)]$$
$$+ \frac{k_{1s}[H_s]_0}{k_2 - k_{1s}}[\exp(-k_{1s} t) - \exp(-k_2 t)] \tag{9}$$

where $[H]$ represents the total xylan concentration; $[H_f]$ and $[H_s]$ are the concentrations of fast and slow hydrolytic xylan, respectively ($[H_{f0}] + [H_{s0}] = [H_0]$); $[X]$ and $[F]$ denote the concentrations of xylose and furfural, respectively ($[X_0] = 0$, $[F_0] = 0$); k_{1f} and k_{1s} are the rate constants of fast and slow xylan hydrolysis, respectively; k_2 is the rate constant of xylose degradation.

Saeman Model   Xylan (H) $\xrightarrow{k_1}$ Xylose (X) $\xrightarrow{k_2}$ Furfural (F)

Biphasic Model

Fast-hydrolysis Xylan(H_f) $\searrow^{k_{1f}}$
$\rightarrow$ Xylose (X) $\xrightarrow{k_2}$ Furfural (F)
Slow-hydrolysis Xylan(H_s) $\nearrow_{k_{1s}}$

For the Saeman model, the hemicellulose hydrolysis is assumed to be homogeneous consecutive pseudo-first-order reactions: xylan is first hydrolyzed to xylose followed by xylose degradation to furfural [25]. For the Biphasic model, the biphasic pattern is assumed to be able to maintain during the whole hydrolysis: one part of the hemicellulose fraction tends to hydrolyze faster (fast hydrolysis) than the other part (slow hydrolysis) [26]. The fast and

Estimation of kinetic parameters to fit these non-linear models for EFB hydrolysis was conducted with MATLAB R 2010b (The MathWorks, Inc., Natick, MA). Accountability of the estimated parameters was evaluated by statistical analysis, with which the determination coefficient (R^2) was obtained. To get the kinetic parameters, fraction factors of 65% and 35% were used for the fast and slow hydrolysis fractions, respectively [24].