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Research Article

Optimization of Two-Step Acid-Catalyzed Hydrolysis of Oil Palm Empty Fruit Bunch for High Sugar Concentration in Hydrolysate

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Getting high sugar concentrations in lignocellulosic biomass hydrolysate with reasonable yields of sugars is commercially attractive but very challenging. Two-step acid-catalyzed hydrolysis of oil palm empty fruit bunch (EFB) was conducted to get high sugar concentrations in the hydrolysate. The biphasic kinetic model was used to guide the optimization of the first step dilute acid-catalyzed hydrolysis of EFB. A total sugar concentration of 83.0 g/L with a xylose concentration of 69.5 g/L and a xylose yield of 84.0% was experimentally achieved, which is in well agreement with the model predictions under optimal conditions (3% H_2SO_4 and 1.2% H_3PO_4, w/v, liquid to solid ratio 3 mL/g, 130°C, and 36 min). To further increase total sugar and xylose concentrations in hydrolysate, a second step hydrolysis was performed by adding fresh EFB to the hydrolysate at 130°C for 30 min, giving a total sugar concentration of 114.4 g/L with a xylose concentration of 93.5 g/L and a xylose yield of 56.5%. To the best of our knowledge, the total sugar and xylose concentrations are the highest among those ever reported for acid-catalyzed hydrolysis of lignocellulose.

1. Introduction

Holocellulose sugars in lignocellulosic biomass are rich sources to produce a variety of products by microbial fermentations. Oil palm empty fruit bunch (EFB), a lignocellulosic waste produced during palm oil extraction, has attracted much attention as an abundant lignocellulosic feedstock especially in Southeast Asia [1, 2]. EFB is composed of cellulose (40–60%), hemicellulose (20–30%), and lignin (10–20%) with xylan being the major component of hemicelluloses [3–5]. The cellulose and hemicellulose (collectively holocellulose) components of EFB can be hydrolyzed to monomer sugars by pretreatment and enzymatic hydrolysis [1, 6].

Dilute acid-catalyzed hydrolysis of lignocellulose is one of the most frequently investigated pretreatment methods due to its promising commercial feasibility [7, 8]. Xylan, the major component of hemicelluloses, is very susceptible to dilute acid treatment due to its amorphous structure compared to the highly crystallized cellulose [7]. After acid-catalyzed hydrolysis, most of hemicellulose components are solubilized in hydrolysate as monomer sugars, leaving the solid fraction comprised primarily of cellulose, which is easily hydrolyzed by cellulases to release glucose.

For fermentation processes, usually a high concentration of sugars is necessary to get high product titer for cost-effective product separation. However, for acid-catalyzed hydrolysis of lignocellulose, the reported sugar concentrations in the hydrolysates were usually at 20–60 g/L [9–11]. These sugar concentrations are far from the industrially accepted levels of over 100 g/L for fermentations [12–14]. To obtain high sugar concentrations in hydrolysate, a low liquid to solid ratio (LSR) is necessary. However, the sugar yield is often reduced at high solid loadings. Therefore, it is very challenging to get high sugar concentrations in hydrolysates but still keep good sugar yields.

Here we report a two-step process for acid-catalyzed hydrolysis of EFB to get high sugar concentrations (>110 g/L)

Seaman model $\quad \text{Xylan } (H) \xrightarrow{k_1} \text{Xylose } (X) \xrightarrow{k_2} \text{Furfural } (F)$

Biphasic model

$$\begin{array}{l} \text{Fast-hydrolysis Xylan } (H_f) \xrightarrow{k_{1f}} \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{Xylose } (X) \xrightarrow{k_2} \text{Furfural } (F) \\ \text{Slow-hydrolysis Xylan } (H_s) \xrightarrow{k_{1s}} \end{array}$$

Scheme 1

in the hydrolysate with reasonable sugar yields. The EFB hydrolysis was simulated by a kinetic model to guide the process optimization. To the best of our knowledge, this is the first report that sugar concentrations of over 100 g/L were directly obtained from acid-catalyzed pretreatment of lignocellulose without any additional concentration steps.

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 overnight before use. EFB compositions were analyzed following the standard procedures of NREL [17]. For getting EFB particles of different sizes, 2 mm, 4 mm, and 8 mm screens were 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 (45 g) was added to 135 mL water containing 1.5–3% (w/v) of H_2SO_4 or 0.6–1.2% (w/v) of H_3PO_4 or both. The temperature was raised to predetermined levels (120–140°C) for hydrolyses. 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 the liquid phase 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, Herculse, CA, USA) at 50°C. The mobile phase was 5 mM H_2SO_4 at 0.65 mL/min.

2.4. Mathematic Description of Kinetic Model. Mathematic models have been widely accepted to describe the kinetics of lignocellulose hydrolysis [18–20]. Our previous study showed that the biphasic model can better describe the acid-catalyzed hydrolysis of xylan in EFB [4] than do the Saeman model [21]. So the biphasic model was selected to guide the optimization of the two-step acid-catalyzed hydrolysis of xylan in EFB. The biphasic model is described as shown in Scheme 1 [22, 23].

This model assumes that one part of the hemicellulose fraction tends to hydrolyze faster (fast hydrolysis) than the other part (slow hydrolysis) [24]. The fast and slow hydrolysis fractions differ only slightly per substrate and typically account for about 65% and 35%, respectively [22]. This kinetic model suggests that acid concentration, temperature, and reaction time should be synergistically adjusted to favor xylose accumulation by minimizing sugar degradation [22, 23]. The mathematical description of this model is as follows [22, 23]:

$$\begin{gathered} \frac{d\left[H_f\right]}{dt} = -k_{1f}\left[H_f\right], \\ \frac{d\left[H_s\right]}{dt} = -k_{1s}\left[H_s\right], \\ \frac{d[X]}{dt} = k_{1f}\left[H_f\right] + k_{1s}\left[H_s\right] - k_2[X], \\ \frac{d[F]}{dt} = k_2[X], \\ [X] = \frac{k_{1f}\left[H_f\right]_0}{k_2 - k_{1f}}\left[\exp\left(-k_{1f}t\right) - \exp\left(-k_2 t\right)\right] \\ + \frac{k_{1s}\left[H_s\right]_0}{k_2 - k_{1s}}\left[\exp\left(-k_{1s}t\right) - \exp\left(-k_2 t\right)\right], \end{gathered} \tag{1}$$

where $[H]$ represents the total xylan concentration; $[H_f]$ and $[H_s]$ are the concentrations of fast and slow hydrolytic xylan, respectively ($[H_f]_0 + [H_s]_0 = [H]_0$); $[X]$ 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.

Estimation of kinetic parameters to fit the nonlinear model 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.

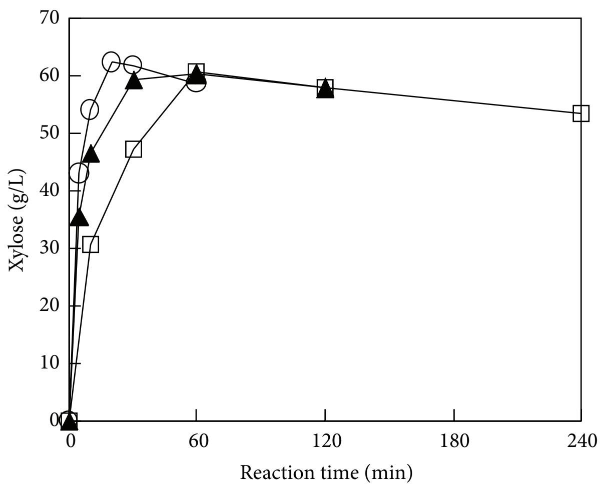

FIGURE 1: Time courses of xylose concentration at different temperatures. □: 120°C; ▲: 130°C; ○: 140°C. Other conditions: 2% (w/v) H_2SO_4 and 0.8% (w/v) H_3PO_4, liquid to solid ratio 3 mL/g.

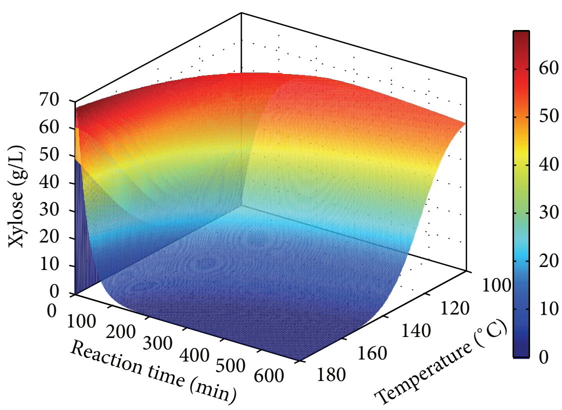

FIGURE 2: Predicted 3-dimentional changes of xylose concentration at different temperatures by biphasic model. Assumed conditions: 2% (w/v) H_2SO_4 and 0.8% (w/v) H_3PO_4, liquid to solid ratio 3 mL/g, 100–180°C.

3. Results and Discussion

3.1. Composition of EFB. The compositions of oven-dried EFB were determined to be 34.3 ± 0.6% of glucan, 21.8 ± 0.3% of xylan, 21.5 ± 0.4% of Klason lignin, and 22.4 ± 1.0% of others [4], which are very similar to those reported by Rahman et al. [1]. The theoretical yield of xylose from EFB was thus calculated to be 24.8 g/100 g EFB. Therefore, the theoretical xylose concentration is 82.7 g/L at a liquid to solid ratio of 3 mL/g.

3.2. Effect of Temperature on EFB Hydrolysis at Low Liquid to Solid Ratio. EFB hydrolysis was first conducted at 120–140°C using 2% (w/v) of H_2SO_4 and 0.8% (w/v) of H_3PO_4 to get the xylose concentration profile in the hydrolysate (Figure 1). The values of k_{1f}, k_{1s}, k_2, and R^2 at different temperatures were obtained using the software MATLAB R 2010b and listed in

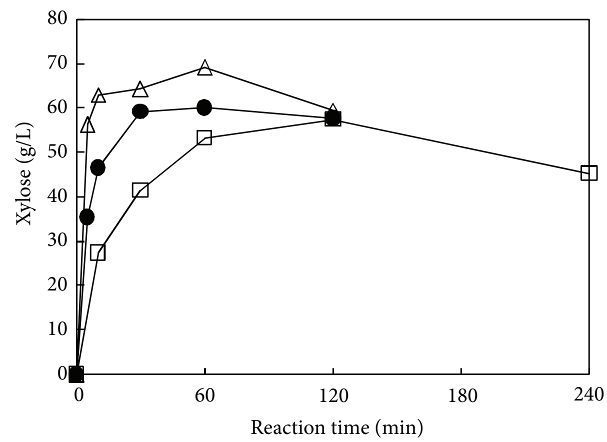

FIGURE 3: Time courses of xylose yield at different acid concentrations. □: 1.5% (w/v) H_2SO_4 and 0.6% (w/v) H_3PO_4; ●: 2% (w/v) H_2SO_4 and 0.8% (w/v) H_3PO_4; △: 2.5% (w/v) H_2SO_4 and 1% (w/v) H_3PO_4. Other conditions: liquid to solid ratio 3 mL/g, 130°C.

Table 1. The rate constants (k_{1f}, k_{1s}, and k_2) in the biphasic model are assumed to follow the classical Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right)\text{min}^{-1}. \tag{2}$$

To obtain E_a, ln(k) was plotted against T^{-1} (data not shown). The E_a values for the fast and slow hydrolysis reactions were calculated to be 89.1 kJ/mol and 99.7 kJ/mol, respectively. Similarly, the E_a value for the sugar degradation reaction was determined to be 73.9 kJ/mol. The E_a values of the fast hydrolysis reaction, slow hydrolysis reaction, and xylose degradation reaction are lower than most of the reported values [23, 25], which might be ascribed to the differences in lignocellulose compositions and acids used. Based on the E_a values obtained above, the k values for the biphasic model can be described as follows:

$$\begin{aligned} k_{1f} &= 5.28\times10^{10}\exp\left(-\frac{89.1}{RT}\right)\text{min}^{-1}, \\ k_{1s} &= 1.18\times10^{11}\exp\left(-\frac{99.7}{RT}\right)\text{min}^{-1}, \\ k_2 &= 1.18\times10^{7}\exp\left(-\frac{73.9}{RT}\right)\text{min}^{-1}. \end{aligned} \tag{3}$$

The predicted results based on the biphasic model are depicted in Figure 2. It is seen that a high reaction temperature leads to an increase in optimal xylose concentration and a decrease in the required reaction time for achieving the highest xylose concentration. High xylose concentrations (>60 g/L) are achievable at 130–180°C.

3.3. Effect of Acid Concentration on EFB Hydrolysis at Low Liquid to Solid Ratio. In order to correlate the kinetic parameters k_{1f}, k_{1s}, and k_2 with acid concentration, experiments were conducted at 130°C to get the required data (Figure 3).

Table 1: Estimated kinetic parameters of biphasic model at different temperatures and acid concentrations.

		k_{1f} (min^{-1})	k_{1s} (min^{-1})	k_2 (min^{-1})	R^2
Temperature (°C)	120	6.92×10^{-2}	7.20×10^{-3}	1.90×10^{-3}	0.990
	130	1.89×10^{-1}	1.27×10^{-2}	2.70×10^{-3}	0.998
	140	2.58×10^{-1}	3.16×10^{-2}	5.70×10^{-3}	0.999
Acid concentration (w/v)	1.5% H_2SO_4 + 0.6% H_3PO_4	5.17×10^{-2}	6.70×10^{-3}	2.60×10^{-3}	0.981
	2% H_2SO_4 + 0.8% H_3PO_4	1.89×10^{-1}	1.27×10^{-2}	2.70×10^{-3}	0.998
	2.5% H_2SO_4 + 1% H_3PO_4	7.56×10^{-1}	3.45×10^{-2}	2.90×10^{-3}	0.995

Table 2: Estimated n and k_0 for k_{1f}, k_{1s}, and k_2.

	n	k_0 (min^{-1})	Slope R^2
k_{1f}	5.22	1.60×10^{28}	0.991
k_{1s}	3.16	3.16×10^{21}	0.961
k_2	0.21	5.20×10^{7}	0.939

The rate constants (k_{1f}, k_{1s}, and k_2) in the biphasic model are assumed to follow the modified Arrhenius equation [23]:

$$k = k_0[H^+]^n \exp\left(-\frac{E_a}{RT}\right) \mathrm{min}^{-1}, \tag{4}$$

where $[H^+]$ (mol/g) represents the number of moles of aqueous hydronium ion per unit weight of EFB. The H^+ concentration was measured to be 0.040 M using 0.5% (w/v) of H_2SO_4 and 0.2% (w/v) of H_3PO_4 as the catalysts. At the liquid to solid ratio of 3 mL/g, $[H^+]$ can be expressed as 4.0 $\times 10^{-5} \times 3$ (mol/g). Therefore, when the acid dosage used is D times of the concentration of using 0.5% (w/v) of H_2SO_4 and 0.4% (w/v) of H_3PO_4, $[H^+]$ can be expressed as $4.0 \times 10^{-5} \times 3 \times D$ (mol/g).

The values of k_{1f}, k_{1s}, k_2, and R^2 were obtained using the software MATLAB R 2010b and listed in Table 1. Then ln(k) was plotted against ln$[H^+]$ (data not shown) to get the n and k_0 values corresponding to k_{1f}, k_{1s}, and k_2 (Table 2).

Based on the above parameters, the k values for the biphasic model can be described as follows:

$$\begin{aligned} k_{1f} &= 1.57 \times 10^{28}[H^+]^{5.22} \exp\left(-\frac{89.1}{RT}\right) \mathrm{min}^{-1}, \\ k_{1s} &= 3.16 \times 10^{21}[H^+]^{3.16} \exp\left(-\frac{99.7}{RT}\right) \mathrm{min}^{-1}, \\ k_2 &= 3.40 \times 10^{6}[H^+]^{0.21} \exp\left(-\frac{73.9}{RT}\right) \mathrm{min}^{-1}. \end{aligned} \tag{5}$$

Now the xylose yields at different acid concentrations can be calculated based on (5) (Figure 4). It is seen that an optimal xylose concentration of 70 g/L is able to be achieved at the liquid to solid ratio of 3 mL/g. The optimal xylose concentration increases with increasing acid concentration. The decrease in reaction temperature does not significantly affect the xylose yield at high acid concentrations. A xylose concentration of 69.5 ± 1.5 g/L (corresponding to a xylose yield of 84.0 ± 1.8%) and a total sugar concentration of 83.0 ± 1.9 g/L in the hydrolysate were experimentally achieved under the optimal conditions (3% H_2SO_4 and 1.2% H_3PO_4, w/v, liquid to solid ratio 3 mL/g, 130°C, and 36 min) as predicted by the biphasic model. The concentrations of acetic acid, furfural, and HMF are 16.2 ± 0.2, 2.3 ± 0.2, and 0.2 ± 0.1 g/L, respectively. The total sugar and xylose concentrations are the highest ever reported for acid-catalyzed hydrolysis of lignocellulose owing to the use of a low liquid to solid ratio under the optimized conditions (Table 3) [1, 9, 11, 15].

3.4. Two-Step Hydrolysis of EFB. To further increase xylose concentration in the hydrolysate, a two-step hydrolysis strategy was applied. Into the hydrolysates obtained at different acid concentrations (2-3% H_2SO_4 and 0.8–1.2% H_3PO_4, w/v) was added fresh EFB for second step hydrolysis under the optimal conditions. The biphasic model predicts the optimal reaction times for the first step as 36 min for 3% H_2SO_4 and 0.8–1.2% H_3PO_4, 49 min for 2.5% H_2SO_4 and 1% H_3PO_4, and 64 min for 3% H_2SO_4 and 0.8–1.2% H_3PO_4, respectively, which were used to prepare the hydrolysates at 130°C and a LSR of 3 mL/g. The hydrolysates thus obtained were then mixed with fresh EFB for hydrolysis at 130°C and a LSR of 3 mL/g for different times. As shown in Figure 5, the xylose concentration was further increased with increasing acid concentration. A total sugar concentration of 114.4 g/L and a xylose concentration of 93.5 g/L with a xylose yield of 56.5% were experimentally achieved under the optimal conditions of 3% (w/v) H_2SO_4 and 1.2% (w/v) H_3PO_4, liquid to solid ratio 3 mL/g, 130°C, and 30 min. The concentrations of acetic acid, furfural, and HMF are 27.4, 8.0, and 0.7 g/L, respectively. These are, to the best of our knowledge, the highest total sugar and xylose concentrations in hydrolysates ever reported for acid-catalyzed hydrolysis of EFB. The two-step hydrolysis increased the xylose concentration compared to the one-step process but at a cost of reduced xylose yield due to the severer sugar degradation. Therefore, a compromise between high sugar concentration and high sugar yield must be considered for practical applications. It is worth mentioning that, during the acid-catalyzed hydrolysis, only hemicellulose sugars are stripped into the hydrolysate while the majority of cellulose is still existing in the solid form as a cellulose-lignin complex, which needs to be further converted to glucose either chemically or enzymatically before it can be utilized as a carbon source for fermentation by most microbes. The maximal glucose concentrations ever reported were in excess of 190 g/L by acid hydrolysis of a hardwood (southern red oak) rather than oil palm empty fruit bunch [26]. The total sugar concentration of 114.4 g/L obtained here is thought to be good enough for most commercial fermentation processes.

Table 3: Comparison of total sugar and xylose concentrations in acid hydrolysate with literature results.

Lignocellulose	Acid	Condition	Total sugars (g/L)	Xylose (g/L)	Reference
Rapeseed straw (*Brassica napus*)	1.76% H_2SO_4 (w/v)	152.6°C, 21 min, 15 mL liquid/g solid	14	10.5	[11]
Sorghum straw	6% HCl (w/w)	122°C, 70 min, 10 g liquid/g solid	20	16.2	[15]
Silvergrass, rice straw, and bagasse	1–3% H_2SO_4 (w/w)	121°C, 10–180 min, 10 mL liquid/g solid	27.9/28.1/29.8	24.2/21.9/21.7	[16]
EFB	2% H_2SO_4 (w/w)	119°C, 60 min, 8 g liquid/g solid	NA*	31.1	[1]
Sugarcane bagasse	3% H_2SO_4	121°C, 40 min, 4 mL liquid/g solid	NA	57.3	[9]
EFB	3% H_2SO_4 and 1.2% H_3PO_4 (w/v)	130°C, 30 min, 3 mL liquid/g solid	83.0	69.5	Step 1 in this study
EFB	Hydrolysate from step 1	130°C, 36 min, 3 mL liquid/g solid	114.4	93.5	Step 2 in this study

*Not available in the reference.

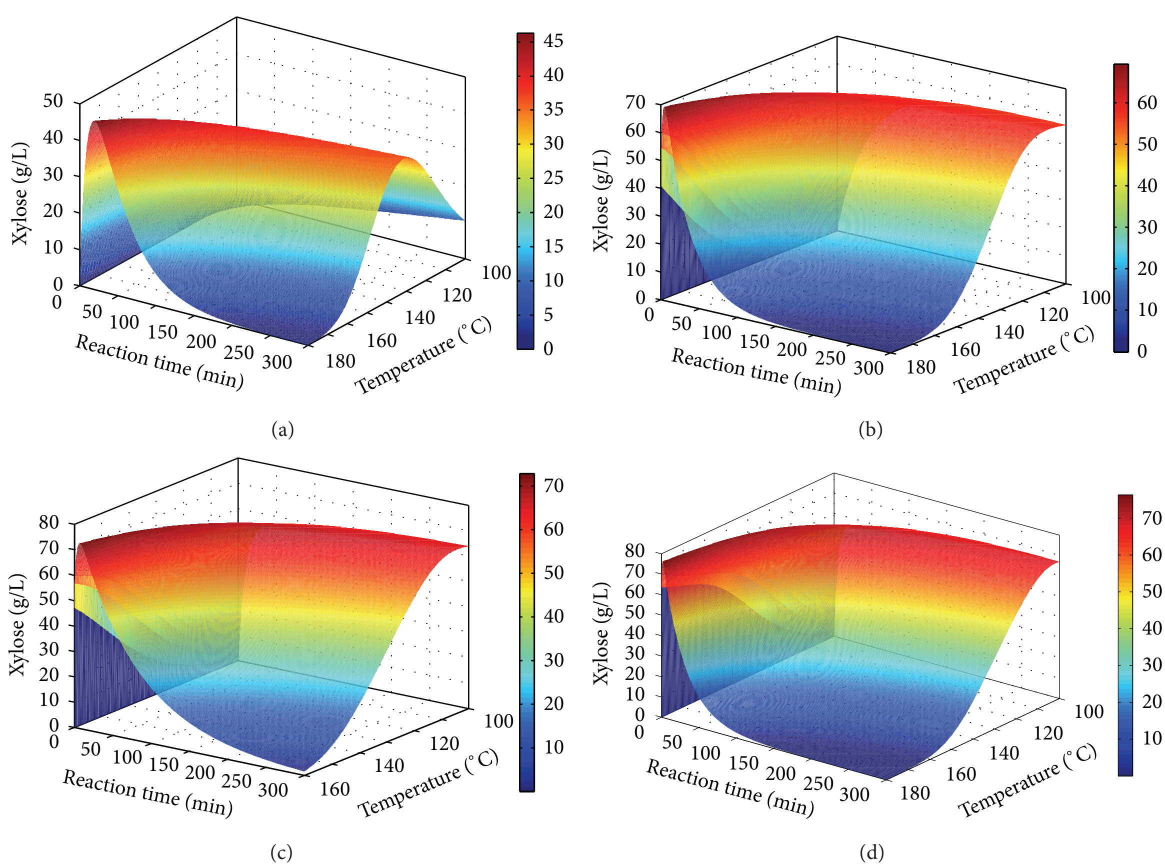

Figure 4: Predicted 3-dimentional changes of xylose concentration at different acid concentrations. (a) 1% (w/v) H_2SO_4 and 0.4% (w/v) H_3PO_4; (b) 2% (w/v) H_2SO_4 and 0.8% (w/v) H_3PO_4; (c) 2.5% (w/v) H_2SO_4 and 1% (w/v) H_3PO_4; (d) 3% (w/v) H_2SO_4 and 1.2% (w/v) H_3PO_4. Other assumed conditions: liquid to solid ratio 3 mL/g, 100–180°C.

4. Conclusions

Two-step acid-catalyzed hydrolysis of EFB at low liquid to solid ratios to get high sugar concentrations in hydrolysates was investigated and optimized based on the biphasic model. A total sugar concentration of 83.0 g/L and a xylose concentration of 69.5 g/L with a xylose yield of 84.0% were experimentally achieved in the first step hydrolysis under the optimal conditions. The total sugar and xylose concentrations were further increased to 114.4 g/L and 93.5 g/L, respectively, in the second step hydrolysis with a total xylose yield of 56.5%. These are, to the best of our knowledge, the highest

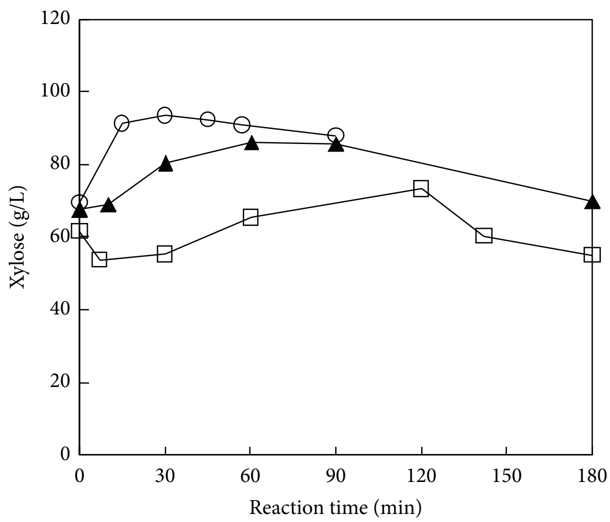

Figure 5: Time courses of xylose concentration in second step EFB hydrolysis at different acid concentrations. □: 2% (w/v) H_2SO_4 and 0.8% (w/v) H_3PO_4; ▲: 2.5% (w/v) H_2SO_4 and 1% (w/v) H_3PO_4; ○: 3% (w/v) H_2SO_4 and 1.2% (w/v) H_3PO_4. Other conditions: liquid to solid ratio 3 mL/g, 130°C.

total sugar and xylose concentrations in hydrolysates ever reported for acid-catalyzed hydrolysis of EFB.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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