

Experimental and Technoeconomic Assessment of Monosaccharide and Furan Production under High Biomass Loading without Solid–Liquid Separation

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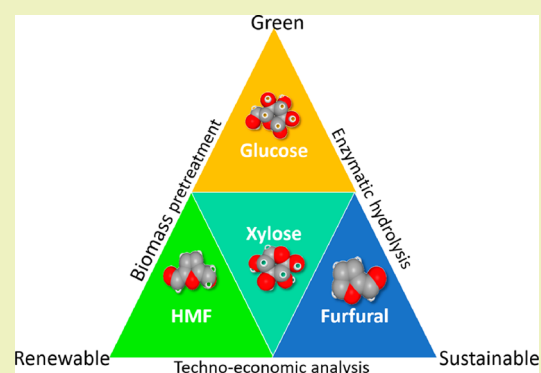
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ABSTRACT: Excessive water and chemicals are often used in biomass valorization because of postpretreatment washing and wastewater treatment. To address this issue, three pretreatment scenarios (I: H₂SO₄ pretreatment with NaOH neutralization; II: NaOH pretreatment with H₂SO₄ neutralization; and III: parallel H₂SO₄ and NaOH pretreatments following their integration) with enzymatic hydrolysis were performed for glucose, xylose, 5-hydroxymethylfurfural (HMF), and furfural production at high solid (15 and 25%, w/v) loading without solid–liquid separation and further detoxification. With an initial solid loading of 25% (w/v), scenario I reached the highest furfural (4.94 g/L) and HMF (2.82 g/L) concentrations, scenario II achieved the highest glucose (73.25%) and xylose (77.49%) yields, while scenario III displayed the highest sugar concentration (74.53 g/L). Only the hydrolysate from NaOH pretreatment and enzymatic hydrolysis with 10% initial solid loading can be efficiently fermented to ethanol (17.92 g/L) by the traditional yeast. Technoeconomic analysis showed that hydrolase unit cost (\$2.00–10.00/kg) notably governs the capital investment and annual operating cost. The lower annual glucose [197.28 thousand metric tons (TMt)] and xylose (52.11 TMt) output with sugar revenue of \$255.05 million for scenario I was compensated by HMF (6.98 TMt) and furfural (10.31 TMt) output with furan revenue of \$80.11 million. Scenario II had the higher annual glucose (208.46 TMt) and xylose (71.19 TMt) output than scenario III (glucose: 206.04 TMt; xylose: 65.32 TMt), but its total revenue (\$286.01 million) was notably lower than scenario III (\$330.71 million). This indicates that furans play a critical role in determining the potential value of the hydrolysate. A sugar minimum selling price of \$2013.23/Mt was achieved by scenario III with the hydrolase unit cost of \$4.00/kg. Sensitivity analyses revealed that the hydrolase unit cost was a dominating factor determining the sugar minimum selling price.

KEYWORDS: High solid loading, Biomass pretreatment, Monosaccharide, Furan, Technoeconomic analysis



INTRODUCTION

Bioproducts derived from lignocellulosic biomass have a great potential to replace fossil-based chemicals and energy materials. To unlock the recalcitrant biomass, thermochemical pretreatment is an inevitably critical step.^{1–5} During pretreatment, cellulose, hemicellulose, and lignin can be partially degraded and solubilized into the liquid fraction.^{1–10} The pretreated solid fraction is often separated from liquid fraction and washed with excessive water and then mixed with a fresh buffer solution for enzymatic hydrolysis, while the resultant liquid fraction is often discarded.^{11,12} This conventional process induces water overconsumption and chemicals loss. The main reason for wastewater disposal is that derivatives (such as acids, furans, and phenols) and residual chemicals (such as acids, alkalis, ionic liquids, organic solvents, and deep eutectic solvents) from initial pretreatment reagents are detrimental to enzymes and strains.^{13–15} For high-cost solvents (such as ionic liquids, organic solvents, and deep eutectic

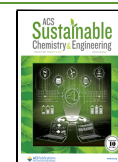
solvents) used for pretreatment, it is cost-effective to recover them from the liquid fraction. In this respect, bioproduct minimum selling price (MSP) was reported to be sensitive to the recycling rates of solvents.^{16,17} Regarding the economic aspects, low-cost dilute sulfuric acid (H₂SO₄) pretreatment is highly recommended by the National Renewable Energy Laboratory (NREL) for commercial development.¹⁸

Low solid loading ($\leq 10\%$, w/v) for biomass pretreatment and enzymatic hydrolysis has been widely used to promote pretreatment technology with the expected higher sugar

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yield.¹⁹ However, from an economic standpoint, maintaining high solid loading is favored due to its envisioned lower water consumption and higher sugar concentration.^{20–22} A review of the literature shows that solid loading used for pretreatment can reach up to 200% (w/v), but enzymatic hydrolysis of the pretreated biomass was commonly performed under 10% (w/v) solid loading to promote the pretreatment technology.^{23–26} Seemingly, these studies have great potential to diminish water consumption, but the phenomenon of excessive water washing and wastewater discarding after pretreatment would contradict the original idea of reducing water consumption. Nevertheless, the side effects such as weak pretreatment effectiveness, inhibitor accumulation, and high slurry viscosity were also observed.^{21,22,27} Batch and fed-batch models have been applied to prompt enzymatic hydrolysis over 50% (w/v) solid loading.^{28–33} In this regard, biomass-water and lignin-enzyme interactions often result in low sugar yield and extend the hydrolysis time, which is recognized as “high-solid side effect”.^{21,22,27,29,34} Herein, the question, whether the higher solid loading used for biomass pretreatment and enzymatic hydrolysis is better, should be taken into consideration. Additionally, guaranteeing mass balance is a prerequisite for continuous industrial production. Therefore, in keeping with the objective of reducing water consumption and production cost, sustaining high solid loading from pretreatment to enzymatic hydrolysis without solid–liquid separation is required. However, few studies have been experimentally investigated this approach.

Technoeconomic analysis (TEA) is an important approach to screen potential research feasibility.^{35,36} Several studies have conducted the TEA of sugar production from lignocellulosic biomass and demonstrated the commercial probability of these biorefineries.^{37–41} However, these TEA studies were predominantly based on empirical simulation. To date, few TEA studies have been conducted on a cellulosic sugar biorefinery that can coproduce higher-value furan according to experimental data.⁴² Therefore, the objective of this work is to fill the gap of knowledge between laboratory and commercialization using the lab-scale results for TEA simulation. To reduce water consumption and chemical loss, three pretreatment methods were experimentally designed and implemented under high solid loading without postwashing, wastewater discarding, and new buffer addition. Pretreatment effectiveness was elucidated by biophysical techniques including scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy as well as compositional analysis. The potential of hydrolysate for yeast fermentation was also illustrated. In addition, a base-case TEA was performed to estimate the feasibility of these biorefineries. This study offered new insights into the engineering synergetic design of biomass-to-bioproducts conversion from the perspective of industrial production.

MATERIALS AND METHODS

Materials. Industrial hemp biomass was harvested from Kansas State University Agricultural Farm (Manhattan, KS). After cutting off branches and leaves, stems were dried at 49 °C for 72 h and then sequentially pulverized by an SM 2000 cutting mill (Restsch Inc. Newton, PA) and kitchen mill (Blendtec Residential, Orem, UT) to achieve size (<2 mm) reduction.^{11,12} Cellulase (Cellic CTec3) and hemicellulase (NS22244) were provided by Novozymes (Franklinton, NC). The chemicals were purchased from Thermo Fisher Scientific Chemicals Inc. (Ward Hill, MA).

Biomass Pretreatment. Biomass was poured into the 75 mL stainless steel reactor (Swagelok, Kansas City Valve & Fitting Co., KS), followed by loading 30 mL of reagent with H₂SO₄ at pH = 1.12, around 0.08 mol/L or NaOH at pH = 13.53, around 0.34 mol/L. The resultant solid loadings (w/v) were 15% (4.5 g-biomass/30 mL-reagent) and 25% (7.5 g-biomass/30 mL-reagent). It should be mentioned that mixing biomass and reagents homogeneously was challenging when solid loading was greater than 25% (w/v). These reactors were instantly immersed into a preheated 190 °C sandbath (Techne Inc., Princeton, NJ) equipped with an air blower for 40 min.^{11,12} After pretreatment, cold tap water was used to quench the further reaction. In order to collect the pretreated slurry, 15 and 7.5 mL of water was poured into the reactors that contained 15% and 25% solid biomass loadings, respectively. For single H₂SO₄ or NaOH pretreatment, the pH of the pretreated slurry was adjusted by 10% (w/w) H₂SO₄ or 10 mol/L NaOH to 4.50, while for combined pretreatment the slurries from H₂SO₄ and NaOH pretreatments were mixed to reach the pH around 4.50.¹² To elucidate the pretreatment effectiveness, the slurry was then filtered into a solid and liquid fraction using vacuum filtration with Whatman filter paper.⁴³ The solid fraction was oven-dried at 49 °C overnight for compositional and structural evaluation, whereas the liquid fraction was ultrafiltered for compositional analysis.

Enzymatic Hydrolysis and Fermentation. 100 μL Cellic CTec3/g biomass and 50 μL NS22244/g biomass were added to the pretreated biomass slurry without solid–liquid separation and further detoxification. These flasks were incubated in an orbital shaker (I2400 Incubator Shaker, New Brunswick, U.S.A.) at 49 °C with an agitation speed of 150 rpm for 72 h.^{44,45} During hydrolysis, 80 μL of supernatant was pipetted every 12 h from each flask for sugar determination. Because the extra water was used to collect the pretreated biomass, the final solid loading of initial biomass relative to solvent became 10% (4.5 g-biomass/45 mL-reagent) and 20% (7.5 g-biomass/37.5 mL-reagent). Additionally, the fermentation potential of hydrolysate from different pretreatment processes was explored. The activated yeast (Ethanol Red, Lesaffre, Milwaukee, WI, U.S.A.) culture was first prepared following our previous study.⁴⁵ The flask containing 10 mL of hydrolysate was inoculated about 5×10^8 cells and then incubated at 37 °C in an orbital shaker (I2400 Incubator Shaker, New Brunswick, U.S.A.) with 150 rpm for 72 h. After fermentation, 80 μL of supernatant was sampled for compositional measurement.

Structural Characterization and Analytical Procedures. Changes in microstructure, crystallinity and chemical bond of biomass before and after pretreatment were determined by S-3500 Scanning Electron Microscope (Hitachinaka, Ibaraki, Japan), Siemens D-5000 Diffractometer (Bruker, Ettlingen, Germany) with Cu–K radiation, and Fourier Transform Infrared Spectroscopy, respectively. In this regard, the parameters and operational details can be found in the previous studies.^{11,12} Chemical composition of the solid fraction was measured following the procedures from the NREL.^{46,47} The concentrations of glucose, xylose, furfural, and HMF in the liquid fraction and hydrolysate were tested by a 1260 high-performance liquid chromatography system (Agilent, Santa Clara, CA) coupled with an HPX-87H organic acid separation column (7.8 × 300 mm²). The temperature of the column and refractive index detector was set at 60 and 45 °C, respectively. Five mM H₂SO₄ buffer with a flow rate of 0.6 mL/min was used as the mobile phase.

Process Simulation. In this study, process design and simulation were performed using the SuperPro Designer software (Version 9, Intelligen Inc., Scotch Plains, NJ, 2017) based on the experimental data. It should be mentioned that only biomass pretreatment at a solid loading of 25% (w/v) was used to develop the techno-economic models. Raw biomass was transported to a horizontal blending tank, which was designed to integrate numerous constituents of biomass executing the processing of feedstocks homogeneous. It was initially screw-conveyed to shredding mill for size reduction and subsequently transferred to the downstream stirred stoichiometric reactor, where biomass was pretreated by dilute H₂SO₄ for scenario I or NaOH for scenario II. Whereas for scenario III the ground biomass was subjected to a two-way uniform flow splitter with the top stream was

dilute H₂SO₄ pretreatment and the bottom stream was NaOH pretreatment and then delivered to the reactor. The stream was assumed to accomplish the aimed pretreatment temperature. After pretreatment, extra water was intended to wash out the pretreated biomass, which is in agreement with the previous study that feedstock pump ability could only be realized at solid loading below 15%.⁴⁸ The concentrated NaOH and H₂SO₄ solution was utilized to adjust the slurry pH for scenario I and scenario II, respectively. While for scenario III the slurries from H₂SO₄ and NaOH pretreatments were combined without pH adjusting. Enzymatic hydrolysis was initiated by adding hydrolase at continuous stoichiometric reactors. Finally, the slurry was subjected to centrifugation, resulting in solid residues and hydrolysate.

Techno-Economic Analysis. The SuperPro Designer software was used to accomplish economic assumptions and models for the three high-solid (25%, w/v) conversion scenarios. The biorefinery was assumed to consume 75 dry metric tons (Mt) of biomass hourly with a total operating time of 7920 h per year. First, the classification of input and output streams was conducted. The unit costs of raw materials and utilities were obtained from the SuperPro Designer database and previous modeling packages (Table 1).^{16,18,49–51}

Table 1. Unit Cost of Raw Materials, Utilities, and Bioproducts^a

item	unit cost
raw materials	
biomass	\$100.00/Mt
sulfuric acid	\$96.00/Mt
sodium hydroxide	\$400.00/Mt
hydrolase	\$2.00–10.00/kg
water	\$0.50/Mt
utilities	
std power	\$0.05/kWh
steam	\$2.60/Mt
steam (high pressure)	\$17.00/Mt
chilled water	\$0.40/Mt
cooling water	\$0.05/Mt
hot water	\$0.05/Mt
bioproducts	
5-hydroxymethylfurfural	\$10000.00/Mt
furfural	\$1000.00/Mt
glucose/xylose	\$1022.73/Mt

^aData were obtained from the SuperPro Designer database and previous studies.^{16,18,49–51}

Monosaccharides (glucose and xylose) are the main products while furans (HMF and furfural) and solid residues were coproducts. Most TEA studies designed the enzymes onsite production or assumed its cost based on per gallon of ethanol,^{17,18,52–55} however, it was reported that the cost of producing enzymes was much higher than that

commonly assumed in the literature.⁵⁶ In this regard, the hydrolase unit cost of \$2.00–10.00/kg was used to elucidate its effect on three scenarios. It has been reported that the current market price of HMF is higher than \$10 000/Mt,⁴⁹ but its price was fixed at \$10 000/Mt in this work. Second, the size and quantity options of main equipment were based on throughput and calculated with a design mode. Equipment purchase cost was acquired using a built-in cost model. In particular, the parameters of reactors and fermenters were referred to a previous NREL report.¹⁸ The other costs related to equipment such as installation, process piping, insulation, and maintenance were calculated based on equipment purchase cost using self-contained databanks in the SuperPro Designer software. Third, the labor costs (general operator was \$69.00/h and reactor operator is \$70.52/h) were calculated with the basic rate was \$30.00/h for the general operator and \$30.66/h for reactor operator, supervision factor was 0.20, benefits factor was 0.40, administration factor was 0.40, operating supplies factor was 0.10, and 70% of work time devoted to process-related activities. Fourth, the annual operating cost and direct fixed capital cost for three scenarios were evaluated using the SuperPro Designer software.

To obtain the sugar MSP, the discounted cash flow rate of return assessment was executed as the selling price of sugar was iteratively altered to guarantee that sugar revenue should be achieved at the break-even point where total bioproduct revenues and total costs were equal. In this respect, the plant lifetime was 30 years with a construction period of 36 months, and 8%, 60%, 32% of total investment costs were allocated to the first, second, and third years, respectively.^{16,18} The project financing debt was 40% with loan interest of 8% for 10 years and the depreciation period was fixed for 7 years. The discount rate was 10% with the federal corporate tax rate of 35%.

RESULTS AND DISCUSSION

Composition of Solid and Liquid Fraction. Table 2 shows the principal chemical composition of raw and pretreated biomass from different pretreatment conditions. Compared to raw biomass, glucan (56.35–64.45%), and lignin (acid-soluble lignin: 1.18–1.59%; acid-insoluble lignin: 18.56–35.48%) contents increased in the pretreated biomass, while xylan (2.41–11.09%) and other (2.88–7.80%) contents decreased. An increase in glucan and decrease in xylan contents of biomass after pretreatment is in agreement with the previous study where hemp and poplar biomass were pretreated by acetic acid or NaOH at solid loading of 10% (w/v) without postwashing and pH adjusting.¹² The relative enhancement of lignin in H₂SO₄ pretreated biomass is because H₂SO₄ pretreatment can induce the pseudolignin formation and marginally solubilize lignin.^{57,58} For NaOH and combined pretreatments, the increase of lignin is possibly attributed to the recondensation of the solubilized lignin which is triggered by pH adjusting. This phenomenon can be verified by the

Table 2. Chemical Composition (%) of Solid Fraction after Pretreatment, pH Adjusting, and Solid–Liquid Separation^a

biomass sample	glucan	xylan	acid soluble lignin	acid insoluble lignin	others ^b
raw biomass	43.12 ± 0.41	13.61 ± 0.06	0.01 ± 0.00	14.40 ± 0.29	28.86 ± 0.76
H ₂ SO ₄ (15%) ^c	64.45 ± 0.02	2.41 ± 0.02	1.59 ± 0.01	28.67 ± 0.02	2.88 ± 0.00
H ₂ SO ₄ (25%)	56.35 ± 0.04	3.31 ± 0.08	1.46 ± 0.02	35.48 ± 0.03	3.41 ± 0.04
NaOH (15%)	61.37 ± 0.04	11.09 ± 0.04	1.18 ± 0.01	18.56 ± 0.01	7.80 ± 0.01
NaOH (25%)	60.74 ± 0.04	10.27 ± 0.01	1.45 ± 0.02	19.27 ± 0.01	7.27 ± 0.05
combined (15%)	62.44 ± 0.11	7.70 ± 0.01	1.23 ± 0.03	24.60 ± 0.05	4.04 ± 0.13
combined (25%)	57.37 ± 0.07	8.03 ± 0.02	1.39 ± 0.01	27.68 ± 0.04	5.53 ± 0.09

^aSolid composition was on a dry basis. Data: means ± standard deviations. Solid–liquid separation was conducted to determine the pretreatment effectiveness, whereas this process was not needed for enzymatic hydrolysis. ^bOther components included residual chemical reagents, degraded sugars, extractives, and mineral substances. ^cIt represented the pretreatment solid loading (w/v).

Table 3. Chemical Composition (g/L) of Liquid Fraction after Pretreatment, pH Adjusting, and Solid–Liquid Separation^a

sample	glucose	HMF ^b	xylose	furfural
H ₂ SO ₄ (15%) ^c	7.85 ± 0.06	1.69 ± 0.02	5.51 ± 0.01	3.36 ± 0.03
H ₂ SO ₄ (25%)	16.53 ± 0.02	2.82 ± 0.06	7.03 ± 0.01	4.94 ± 0.12
NaOH (15%)	0.25 ± 0.12	nd ^b	0.64 ± 0.00	nd
NaOH (25%)	0.52 ± 0.02	nd	1.28 ± 0.00	nd
combined (15%)	4.49 ± 0.00	0.77 ± 0.01	3.01 ± 0.00	1.62 ± 0.03
combined (25%)	7.59 ± 0.00	1.17 ± 0.02	5.72 ± 0.02	2.23 ± 0.05

^aData: means ± standard deviations. ^bHMF: 5-hydroxymethylfurfural. nd: not detected. ^cIt represents the pretreatment solid loading (w/v).

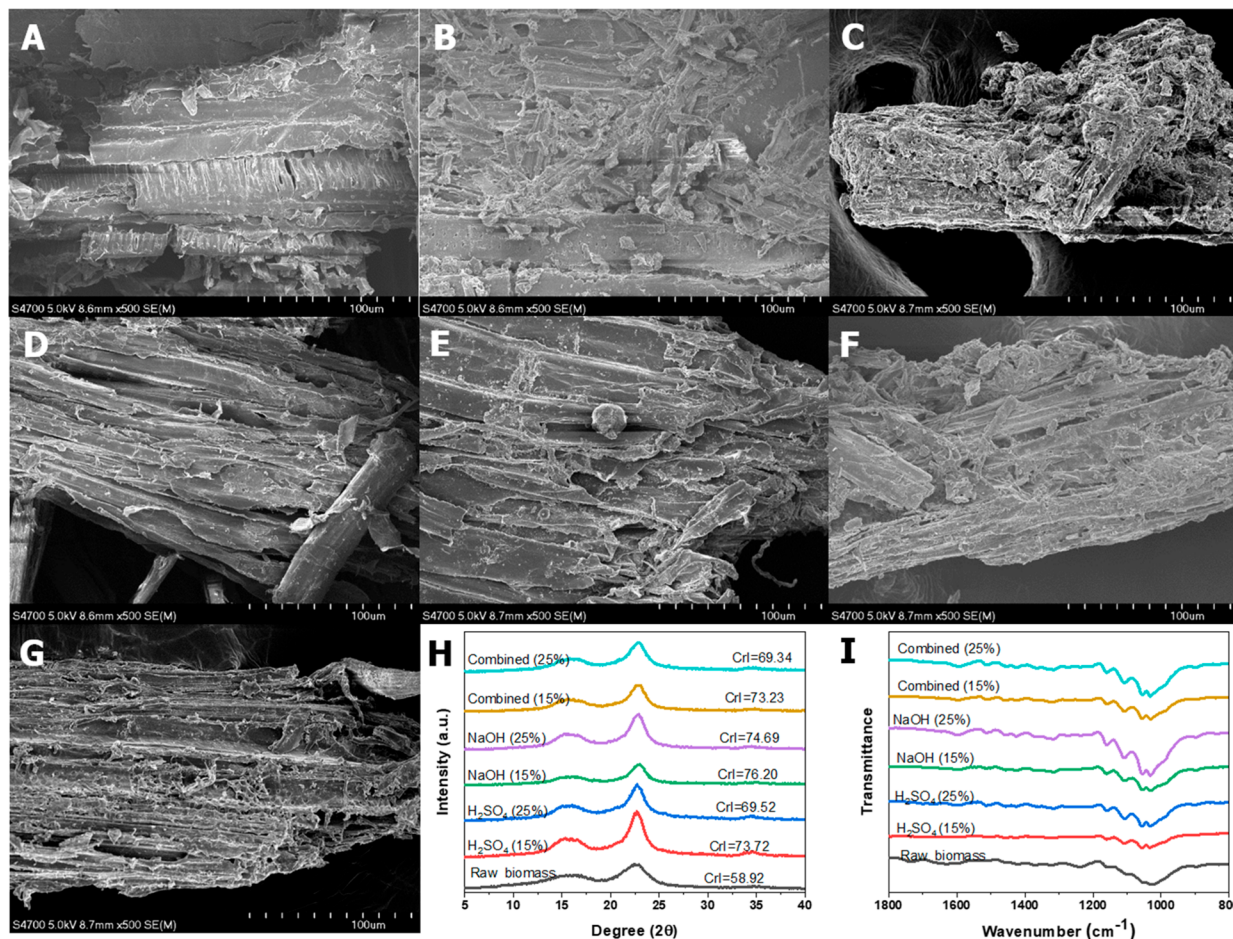


Figure 1. SEM of raw (A) and pretreated biomass (B: H₂SO₄-15%; C: H₂SO₄-25%; D: NaOH-15%; E: NaOH-25%; F: Combined-15%; G: Combined-25%) as well as their XRD (H) and FTIR (I) properties.

previous finding that NaOH pretreated rice straw followed by acidification with hydrochloric acid showed higher lignin content and lower lignin removal than that without acidification.⁵⁹ In addition, the removal of xylan and extractives from biomass during pretreatment can relatively increase glucan and lignin contents in the pretreated biomass. It was also noticed that H₂SO₄ can catalyze degradation of hemicellulose more than NaOH (2.41–3.31% vs 10.27–11.09%). As pretreatment solid loading increased from 15% to 25% (w/v), glucan in pretreated biomass decreased while lignin increased. This trend is in accordance with the report that glucan decreased from 51.40 to 36.20% and lignin increased from 7.50 to 10.60% in aqueous ammonia pretreated corn stover without washing as the pretreatment solid loading increased from 10 to 25% (w/w).⁶⁰

Table 3 shows the concentrations of monosaccharides and derivatives in the liquid fraction from different pretreatment conditions. H₂SO₄ pretreatment significantly disrupted more glucan and xylan into the liquid fraction than NaOH pretreatment, which can be reflected by the higher glucose (7.85–16.53 g/L) and xylose (5.51–7.03 g/L) concentrations. Correspondingly, high monosaccharides availability is often accompanied by their further degradation with HMF (1.69–2.82 g/L) and furfural (3.36–4.94 g/L) formation. When the H₂SO₄ and NaOH pretreated slurries were combined, the concentrations of sugar (glucose and xylose) and its derivatives (HMF and furfural) in the liquid fraction were almost halved compared to H₂SO₄ pretreatment. As pretreatment solid loading increased from 15% to 25% (w/v), monosaccharides and derivatives were approximately doubled. Toquero and Bolado conducted four different pretreatments of wheat straw

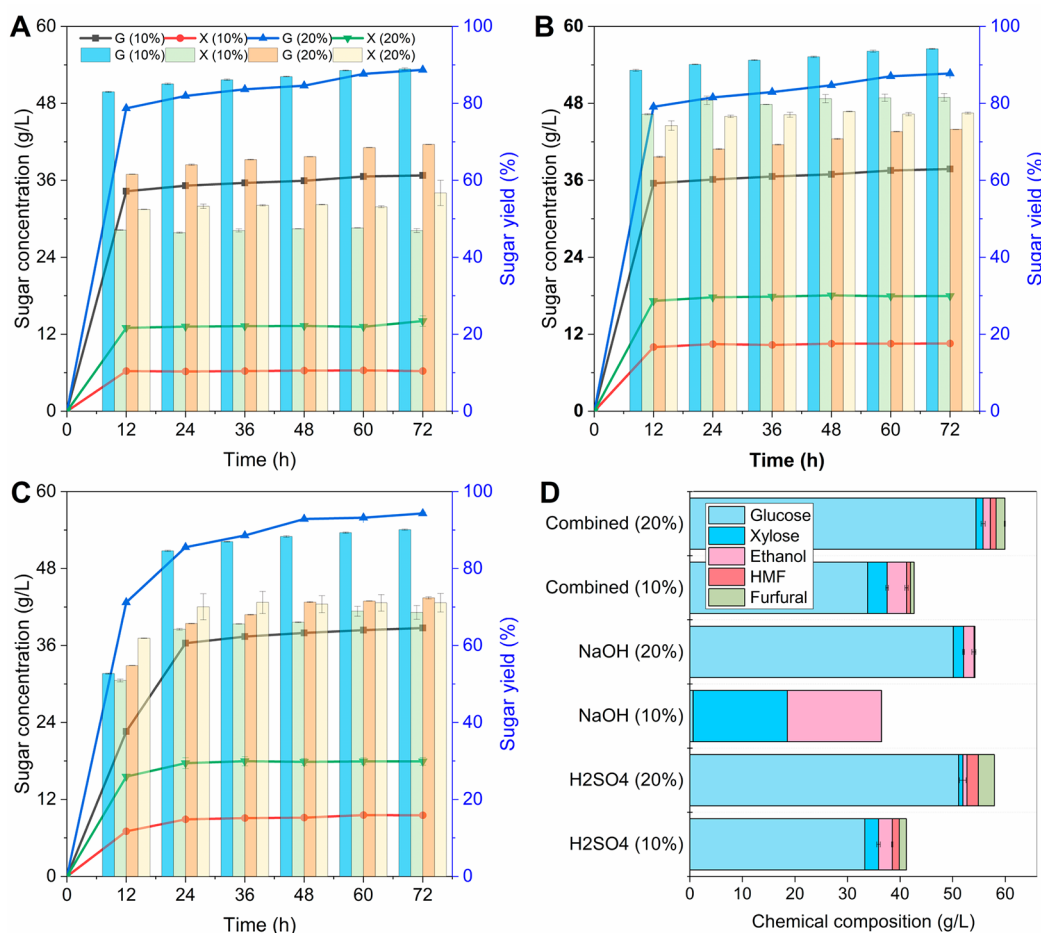


Figure 2. Glucose and xylose concentrations (line) and total yields (column) from enzymatic hydrolysis of H_2SO_4 (A), NaOH (B), and combined pretreated (C) biomass at different solid loadings as well as the compositional profile (D) of the hydrolysate after 72-h fermentation with the traditional yeast.

with 10% (w/w) solid loading and reported 0.67–2.26 g cellulose and 0.81–16.49 g hemicellulose/100 g raw material in the liquid fraction.⁶¹ However, the liquid fraction was not used for enzymatic hydrolysis and fermentation.⁶¹ If these high-value furans and sugars in the liquid fraction are discarded in industrial production, then there would be a huge economic loss.^{11,12}

Structural Characterization of Raw and Pretreated Biomass. Microstructural, crystalline, and chemical bond properties of raw and pretreated biomass are characterized in Figure 1. SEM is indirectly able to reflect the pretreatment mechanism through tracking the morphological change of biomass.⁴⁵ It was observed that pretreatment amplified surface unevenness compared to raw intact lamellar structures (Figure 1A–G). The small particles on the surface of pretreated biomass might be the agglomerated lignin units which became insoluble after pH adjusting.¹¹ H_2SO_4 pretreated biomass showed irregular micropores (Figure 1B,C) that could derive from the decomposition of hemicellulose.⁴⁵ Whereas NaOH pretreatment altered the sealed skeleton of biomass due to the solubilization of lignin (Figure 1D,E).

The XRD spectrum and CrI values of raw and pretreated biomass are shown in Figure 1H. Pretreatment increased the CrI values of biomass from 58.92 to 76.20%, and the CrI values from solid loading of 15% (73.23–76.20%) were higher than those from solid loading of 25% (69.34–74.69%). These were

attributed to the increase in glucan content.^{11,12,45} Under the same solid loading, NaOH pretreated biomass displayed higher CrI values than H_2SO_4 pretreated biomass, indicating that H_2SO_4 significantly altered the cellulose. FTIR spectra showed that glucan [1091 cm^{-1} (C–O vibration), 1051 cm^{-1} (C–O stretching), and 1023 cm^{-1} (C–O–C pyranose ring skeletal vibration)] and lignin [1514 cm^{-1} (aromatic skeleton) and 1319 cm^{-1} (syringyl and guaiacyl lignin units)] related peak intensity in pretreated biomass were stronger than raw biomass. This was in agreement with the change of glucan and lignin contents in biomass.¹²

Sugar Concentration and Yield from Enzymatic Hydrolysis. Sugar concentrations and yields from enzymatic hydrolysis of the pretreated biomass slurry without solid–liquid separation and detoxification at different solid loadings are presented in Figure 2. Regardless of which pretreatment methods were applied, increasing solid loading significantly increased the final glucose (52.66–56.59 g/L vs 36.76–38.74 g/L) and xylose (14.06–17.98 g/L vs 6.27–10.56 g/L) concentrations, but the corresponding glucose yields (88.93–94.16% vs 69.32–73.25%) notably decreased. However, xylose yield showed a different trend: it increased for H_2SO_4 and combined pretreatments (Figure 2A,C) but decreased for NaOH pretreatment (Figure 2B). Generally, as solid loading increases, the sugar conversion efficiency gradually decreases due to the low accessibility of enzymes and the cross-linking of

lignin and enzymes.^{11,62,63} Surprisingly, xylose yields for H₂SO₄ and combined pretreatments increased, which is possibly ascribed to that 25% of solid loading used for pretreatment has a relatively less percentage of xylan degradation than 15% of solid loading. This can be indirectly reflected by the higher xylan content in their pretreated biomass (Table 2). Overall, the highest total sugar concentration (glucose: 56.59 g/L; xylose: 17.94 g/L) and yield (10% of solid loading: glucose of 94.16% and xylose of 81.56%; 20% of solid loading: glucose of 73.25% and xylose of 77.49%) were obtained from combined pretreatment (Figure 2C) and NaOH pretreatment (Figure 2B), respectively. Because in this work sugar yield was calculated based on the initial biomass, high sugar yield derived from NaOH pretreatment was associated with its lower sugar degradation during pretreatment.^{44,45} These findings also indicate that calculating sugar yield based on the pretreated biomass would result in overestimating the effect of pretreatment because the monosaccharides derived from glucan and xylan in the liquid fraction are often discarded.

Potential of Hydrolysate for Ethanol Fermentation.

The possibility of hydrolysate from different hydrolysis conditions for ethanol fermentation by the traditional yeast was examined (Figure 2D). Several studies have assumed the feasibility of H₂SO₄ pretreated slurry for ethanol fermentation after pH adjusting without solid–liquid separation and detoxification.^{18,52,64} However, the present study showed that only the hydrolysate from NaOH pretreatment and enzymatic hydrolysis with 10% initial solid loading can be efficiently fermented to ethanol (17.92 g/L) by the traditional yeast. The fatal damage of hydrolysate to yeast can be attributed to inhibitory compounds such as HMF, furfural, and phenols.^{13,65} It has been reported that methyl isobutyl ketone (MIBK) has excellent furan extraction properties than other water-immiscible organic solvents in the biphasic system.^{66,67} However, if MIBK is used for furan extraction from hydrolysate in this work, it will be difficult to recover it completely from the aqueous phase because of its solubility in water (1.9g/100 mL at 20 °C) and boiling point (117 °C). In addition, a high ratio of MIBK to the aqueous phase is required to achieve the efficient partition coefficient, which would make it economically unfeasible to distill low-concentration HMF (boiling point of 114–116 °C) and furfural (boiling point of 162 °C) from MIBK. Although the pathway of converting sugar to ethanol in this work has encountered technological obstacles, monosaccharides (glucose and xylose) in the hydrolysate can be used as important intermediates for the conversion of high-value chemicals.^{67–71}

Direct Fixed Capital and Total Investment. The breakdown of direct fixed capital and total capital investment for three scenarios is exhibited in Table 4. Scenario II had a considerably higher total plant direct cost (\$105.03 million) than scenarios III (\$76.04 million) and I (\$70.79 million), due to its higher equipment purchase cost. Correspondingly, the cost related to equipment such as process piping, instrumentation, buildings, and auxiliary facilities from scenario II was expectedly higher than those from scenarios I and III. In terms of total plant indirect cost, the engineering and construction costs for scenarios I and III were similar but notably lower than scenario II. During process simulation, the contractor's fee and contingency were also included by SuperPro Designer. Collectively, scenario II still presented a higher direct fixed capital cost of \$193.26 million than those of scenario I (\$130.25 million) and III (\$139.91 million). In contrast,

Table 4. Direct Fixed Capital and Total Investment (\$million) of Three Scenarios

category	scenario I	scenario II	scenario III
equipment purchase cost	21.96	32.60	23.59
installation	7.54	11.16	8.09
process piping	7.69	11.41	8.26
instrumentation	8.79	13.04	9.44
insulation	0.66	0.98	0.71
electrical	2.20	3.26	2.36
buildings	9.88	14.67	10.62
yard improvement	3.29	4.89	3.54
auxiliary facilities	8.79	13.04	9.44
total plant direct cost	70.79	105.03	76.04
engineering	17.70	26.26	19.01
construction	24.78	36.76	26.61
total plant indirect cost	42.47	63.02	45.62
contractor's fee	5.66	8.40	6.08
contingency	11.33	16.81	12.17
direct fixed capital cost^a	130.25	193.26	139.91
working capital	50.74	51.089	50.95
startup cost	6.51	9.66	7.00
total capital investment^b	187.50	254.01	197.86

^aDirect fixed capital cost included total plant direct and indirect costs as well as engineering and construction fees. ^bTotal capital investment comprised direct fixed capital cost, working capital, and startup cost. The capital investment of scenarios was based on hydrolase unit cost of \$4.00/kg.

Brandt et al. reported the fixed capital cost of \$95.00 million for nonconcentrated sugar production from softwood (24.90 TMT/year) using three-stage milling as pretreatment.³⁸ Counting the working capital and startup cost, the total capital investment of \$187.50 million for scenario I, \$254.01 million for scenario II, and \$197.86 million for scenario III were obtained based on hydrolase unit cost of \$4.00/kg. It was found that hydrolase unit cost had only a linear correlation with working capital (Figure 3A–C), which indicates that the hydrolase unit cost will affect the total capital investment through working capital. For example, if the hydrolase unit cost was \$10/kg, the total capital investment for scenarios I, II, and III reached up to \$248.73 million, \$315.25 million, and \$259.09 million, respectively. In other studies, the capital investment of biomass-to-sugar biorefinery was highly associated with biomass consumption capacity, energy recovery, and process design.^{38,72}

Annual Operating Cost Breakdown. Results showed that hydrolase unit cost had a greater impact on the annual operating cost of three scenarios through affecting the cost of raw materials by linear (Figure 3D–F). As the hydrolase unit cost increased from \$2.00/kg to \$10.00/kg, the annual operating cost from three scenarios significantly enhanced from \$363.91 million to \$1280.37 million. This made the cost of raw materials the dominant contributor to the annual operating cost (Figure 3D–F). With the same hydrolase unit cost, annual operating cost followed the order of scenario II > scenario III > scenario I (Figure 3D–F). Explicitly, the main contribution to the difference among the scenarios was facility-dependent because \$44.30 million from scenario II was significantly higher than \$32.07 million from scenario III and \$29.85 million from scenario I. Scenarios I (\$32.85 million) and II (\$32.46 million) had similar utilities cost, but they were notably lower than scenario III (\$38.67 million).

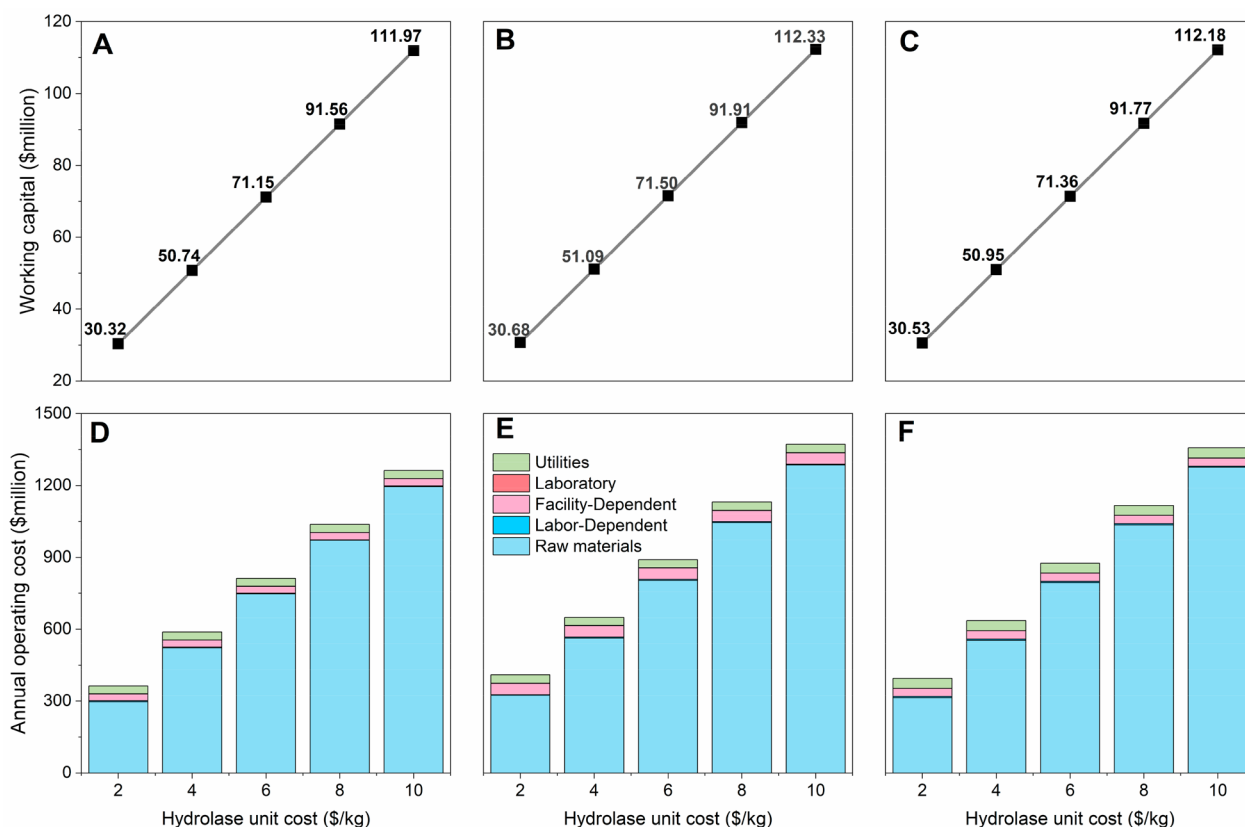


Figure 3. Effects of hydrolase unit cost on working capital (A–C) and annual operating cost breakdown (D–F) of scenarios I (A and D), II (B and E), and III (C and F).

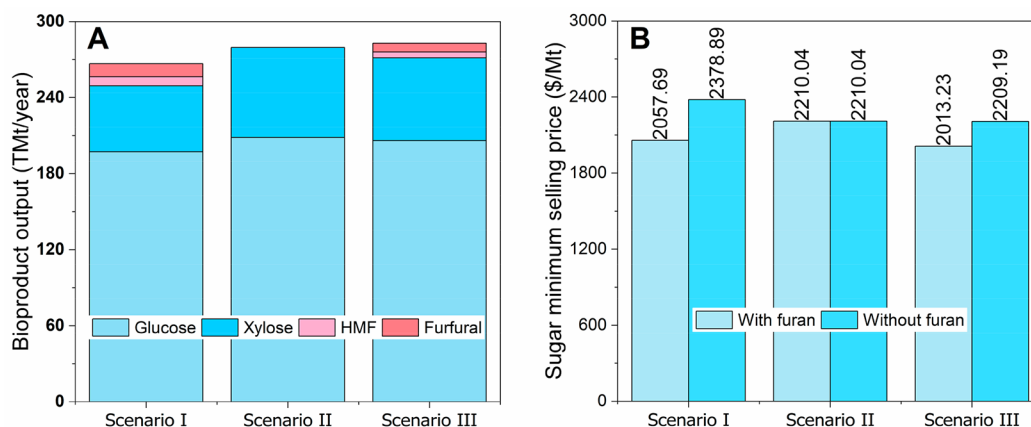


Figure 4. Bioproduct annual output (A) and sugar minimum selling price with/without considering furan (B) as a portion of the revenue under the hydrolase unit cost of \$4.00/kg.

Potential Value of Bioproducts and Sugar Minimum Selling Price. Sugar annual output followed the order: scenario II (208.46 TMT of glucose and 71.19 TMT of xylose) > scenario III (206.04 TMT of glucose and 65.32 TMT of xylose) > scenario I (197.28 TMT of glucose and 52.11 TMT of xylose) (Figure 4A). Whereas furan annual output showed the opposite trend: scenario I (6.98 TMT of HMF and 10.31 TMT of furfural) > scenario III (4.63 TMT of HMF and 6.88 TMT of furfural) > scenario II (no furan formation) (Figure 4A).

According to the bioproduct unit cost (Table 1), the annual revenue for scenario I (\$335.16 million) was higher than scenarios II (\$286.01 million) and III (\$330.71 million) (Figure 5). Although scenario II showed the highest sugar

revenue (glucose: \$213.20 million; xylose: 72.81 million) (Figure 5B), the lower sugar revenue for scenarios I (glucose: \$201.76 million; xylose: 53.29 million) and III (glucose: \$210.73 million; xylose: 66.80 million) was compensated by the higher furan revenue (scenario I: \$69.80 million for HMF and \$10.31 million for furfural; scenario III: \$46.30 million for HMF and \$6.88 million for furfural) (Figure 5A,C). Moreover, the low furan annual output accounted for 23.90% (scenario I) and 16.08% (scenario III) of total revenue (Figure 5A,C). These findings indicate that it is not advisable to blindly pursue the high sugar yield via discarding the high-price degradation products.^{11,12}

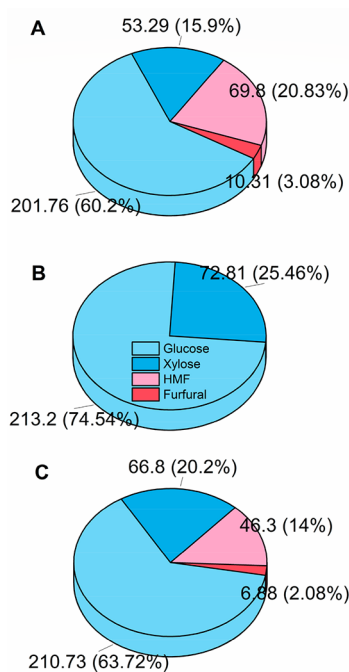


Figure 5. Bioproduct annual revenue (\$million) and breakdown (percentage) of scenarios I (A), II (B), and III (C).

Figure 4B shows the sugar MSP from three scenarios with/without considering the furan as a portion of the revenue. It can be noticed that furan played a crucial role in reducing the sugar MSP from \$2378.89/Mt to \$2057.69/Mt for scenario I and from \$2209.19/Mt to \$2013.23/Mt for scenario III (Figure 4B). Considering furan's income, scenario II yielded the highest sugar MSP of \$2210.04/Mt than scenarios I and III. This also suggests that the higher total capital investment (Table 4) and annual operating cost (Figure 3D–F) offset the advantage of high sugar yield to a certain extent. On the basis of the findings in the present study, two perspectives can be extracted: (1) While chasing high biomass-to-bioproduct yield the cost input such as chemical and equipment as well as byproduct potential value should be evaluated in balance; and (2) multistream valorizing lignocellulosic biomass can preserve the advantages and compensate for the disadvantages. In contrast, Ou et al. assumed the enzyme unit cost of \$5.38/kg

protein and reported that the sugar MSP decreased from \$446/Mt to \$347/Mt with xylitol production from hemicellulose and further reduced to \$342/Mt if lignin was utilized for polyol production.³⁷ Brandt et al. used a three-stage milling process of softwood to reach the sugar MSP of \$496/Mt with the enzyme cost of \$3.2 million annually.³⁸

Sensitivity Analysis. Given the uncertainty and immaturity of the current biorefineries, it is essential to understand the impact of the key unit cost of raw material and selling price of byproduct on sugar MSP via a sensitivity analysis (Figure 6). It is observed that the sugar MSP was most sensitive to the hydrolase unit cost. A 20% decrease in hydrolase unit cost led to a significant decline of sugar MSP to \$1692.21/Mt for scenario I, \$1884.12/Mt for scenario II, and \$1677.34/Mt for scenario III. While a 20% increase in biomass cost increased sugar MSP to \$2423.17/Mt for scenario I, \$2535.96/Mt for scenario II, and \$2349.10/Mt for scenario III (Figure 6). Moreover, on cutting biomass unit cost by 20%, sugar MSP was slightly boosted to \$2106.04/Mt for scenario I, \$2253.15/Mt for scenario II, and \$2057.65/Mt for scenario III, whereas a 20% increase in it reduced sugar MSP to \$2009.35/Mt for scenario I, \$2166.93/Mt for scenario II, and \$1968.79/Mt for scenario III. For scenarios I and III, sugar MSP was slightly sensitive to selling prices of solid residues and HMF (Figure 6A,C). Overall, sugar MSP was highly independent of H₂SO₄ and NaOH unit costs as well as the furfural selling price for all scenarios (Figure 6), which is credited to their low shares in terms of total annual operating cost and bioproduct annual revenue, respectively.

CONCLUSIONS

Three scenarios were experimentally implemented for monosaccharides and furans production at high solid loading without solid–liquid separation and detoxification. Increasing pretreatment solid loading boosted the concentration of derivatives but relatively reduced sugar decomposition per unit. Only the hydrolysate from NaOH pretreatment and enzymatic hydrolysis at initial 10% solid loading was able to be efficiently fermented to ethanol by the traditional yeast. Scenario I achieved the highest furan production but the lowest sugar concentrations. Scenario II reached the highest sugar yield without furan formation. Scenario III showed the highest sugar concentration with a moderate concentration of furan. TEA results showed that hydrolase unit cost had

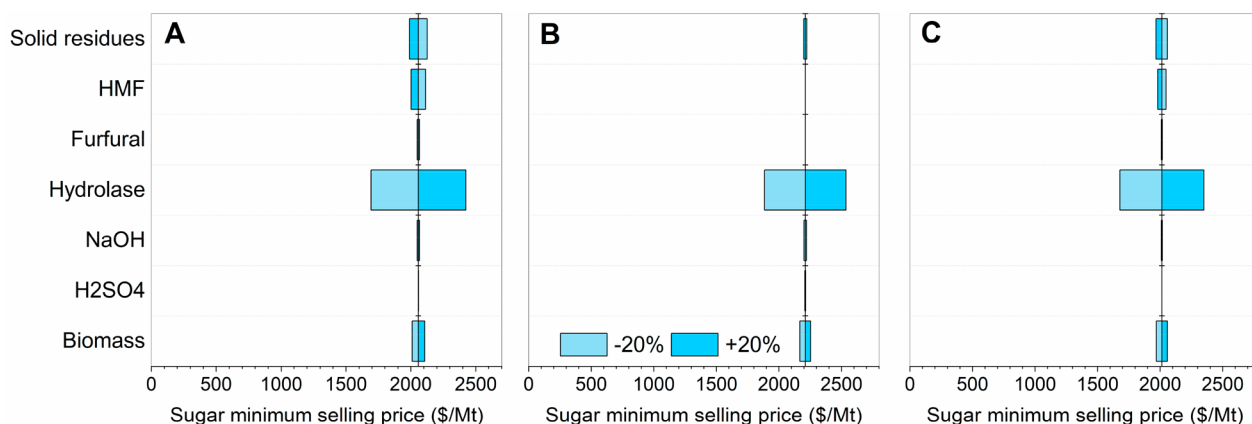


Figure 6. Sensitivity analysis of sugar MSP to unit costs of other materials and selling prices of coproducts (−20%, +20%) for three scenarios (A: scenario I; B: scenario II; and C: scenario III).

significant influences on total capital investment and annual operating cost. Low sugar revenue for scenario I was considerably compensated by the high-value furan income. Although scenario II had the highest sugar annual output, its total revenue was the lowest. Furans played an important role in determining the sugar MSP, as the lowest sugar MSP of \$2013.23/Mt was reached by scenario III. Sensitivity analysis presented that sugar MSP was most sensitive to hydrolase unit cost for all scenarios.

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Author Contributions

J.Z. performed experimental design and wrote the manuscript. J.L. wrote and revised the manuscript. Y.Y. and M.Z. revised the manuscript. K.R. provided biomass and revised the manuscript. D.W. supervised and revised the manuscript. All authors have approved the final version of the manuscript.

Notes

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