

Two-Stage Hydrothermal Liquefaction of Sweet Sorghum Biomass—Part 1: Production of Sugar Mixtures

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Supporting Information

ABSTRACT: A two-stage hydrothermal liquefaction (HTL) process was developed for sweet sorghum biomass to improve carbon conversion, to avoid repolymerization reactions between hemicellulose and lignin derivatives that impair the yield of HTL biocrude oil, and to improve the quality of upgraded biocrude oil while producing sugar mixtures as coproducts. In this paper, the first-stage HTL experiment was carried out using sweet sorghum bagasse at various temperature and time conditions to produce sugar mixtures. Under the optimum conditions of 170 °C and 60 min, 94.1% of hemicellulose and 49.2% cellulose, respectively, were hydrolyzed into C5 and C6 sugars with the maximum sugar yield of 28.14% at the concentration of 28.52 g/L. The sugar stream can be used as a stand-alone or blended with sorghum juices to produce either biofuels or value-added chemicals and products. The remaining solids fraction mainly consisted of lignin, cellulose, and a trace amount of hemicellulose that can be further converted for use as a high-quality biocrude oil.

1. INTRODUCTION

The disparity between dwindling reservation of fossil fuels and increasing global energy demand challenges our society to search for alternative energy sources. In addition, climate change driven by increased greenhouse emissions, economic conflicts, and national energy security further necessitates a need for exploring sustainable drop-in fuels. In this context, lignocellulosic biomass plays an important role in manufacturing both hydrocarbon fuels and industrial chemicals and products. In the United States, approximately one billion tonnes of lignocellulosic biomass could be sustainably produced every year and can be utilized to offset 43% of the total domestic petroleum consumption.¹ Among various lignocellulosic biomass types, energy crops such as sorghum can be grown in marginal lands with low inputs and can be effectively utilized to produce both biofuels and biochemical. Sorghum is a typical C4 annual energy crop and widely planted in the southern regions of the United States with an average yield potential of 20 Mg/ha.² Among different traits of sorghum (grain sorghum, energy sorghum, and sweet sorghum), sweet sorghum is one of the leading energy crops, because of high sugar content and ease of extraction from the plants for biofuels applications.³ Sweet sorghum could accumulate juices up to 78% of the total biomass and the juice is rich in sucrose, which can be directly converted to fuels and chemicals.³ After juice extraction, the remaining biomass is called bagasse, which has ~60%–80% moisture content and can be directly converted to biofuel/chemical intermediates using the hydrothermal liquefaction technology.⁴

Hydrothermal liquefaction (HTL) is a thermochemical technology to directly convert high-moisture feedstock into renewable biofuels in the presence of subcritical water at moderate temperature (280–370 °C) and high pressure (10–25 MPa).⁵ The conventional, whole-stage HTL process produces a biocrude oil that contains many small molecules and oxygenated compounds from structural carbohydrates

hindering the biocrude oil yield and impairing the quality of upgraded biocrude oil after hydrodeoxygenation (HDO).^{6–8} For example, the hemicellulose content in the energy crops is ~20–40 wt %; however, it only contributes to ~5% of the biocrude oil yield, and a majority of its byproducts reaches in the aqueous fraction, rich in carboxylic acids.⁶ In addition, cross reactions between derivatives of hemicellulose (e.g., furfurals) and lignin (e.g., phenolics) produces acid-insoluble solid residues through repolymerization.⁷ The cross reaction between intermediates reduces the biocrude oil yield and poses further challenge during upgrading. Therefore, the hemicellulose present in the biomass could be separated prior to the HTL process.

Currently, hemicellulose in the biomass can be fractionated by hydrolysis using enzymes or dilute acids or bases. However, the cost of enzymatic hydrolysis limits the C5 sugar production at an industrial scale from hemicellulose. Meanwhile, acid or base catalytic hydrolysis requires an additional downstream separation step to remove any mineral catalyst before the utilization of oligomer and monosaccharides from hemicellulose. On the other hand, the HTL process can be used to selectively hydrolyze hemicellulose in the biomass.⁹ During the HTL process, only water, which is the least-expensive solvent, is employed under subcritical conditions to break the glycosidic $\beta(1 \rightarrow 4)$ bond between sugar monomers in hemicellulose, thus, reducing the cost of hydrolysis and simplifying the subsequent separation process. The low-temperature HTL (200–275 °C) process was studied with subcritical water to hydrothermolyze hemicellulose and extract lignin using continuous or semicontinuous reactors.^{10,11} Stahl et al. reported that all hemicellulose was hydrolyzed from pine wood in subcritical water at 240 °C, concomitant with 35% of

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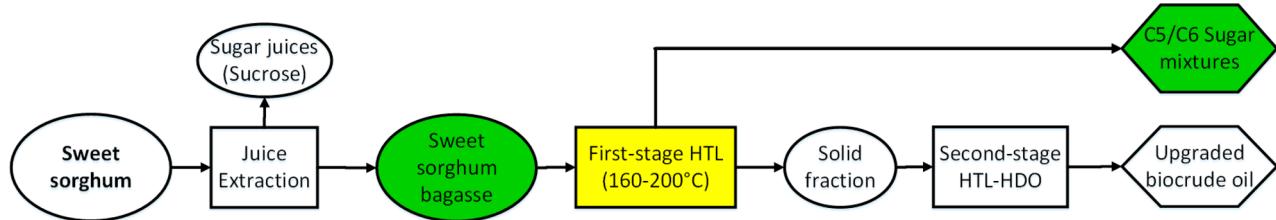


Figure 1. Schematic of first-stage HTL in a two-stage HTL-HDO process.

lignin dissolved.¹² It was also reported that 95% of hemicellulose could be hydrolyzed under HTL conditions of 200 °C, 34.5 MPa for 2 min,¹³ into C5 sugars and oligomers with a recovery yield of 82%.¹⁴ The optimum reaction conditions for hemicellulose hydrolysis were recently investigated using a severity factor in the range from 3.4 to 4.0 with the maximum C5 sugar yield at a severity factor of 3.9.¹⁵ During this hydrothermal hydrolysis process, a fraction of amorphous cellulose also hydrolyzed into glucose (C6 sugar), depending upon the HTL temperature conditions. Nazeri et al. systematically investigated the effect of subcritical water on cellulose hydrothermolysis and provided the mechanism of organic acids formation when the temperature increased from 200 °C to 275 °C.¹⁶ The mixture of C5 and C6 sugars from lignocellulosic biomass is an ideal feedstock for bioethanol cofermentation.^{17,18} It could also be used as a feedstock for the production of platform chemicals of hydroxymethylfural (HMF), furfural, and liquid alkanes (C7 and C15 alkanes) and further derivative into solvents, resins, flavoring agents, pharmaceuticals, and fuel additives.^{19–23}

So far, there has been no attempt made toward a multifaceted approach to HTL technology to simultaneously utilizing all fractions of high-moisture biomass into hydrocarbons-concentrated biocrude oil and sugar mixtures production. In this study, we developed a two-stage hydrothermal liquefaction (HTL) process for sweet sorghum biomass to improve carbon conversion, to avoid repolymerization reactions between hemicellulose and lignin derivatives that impairs the yield of HTL biocrude oil and to improve the quality of upgraded biocrude oil while producing sugar mixtures as coproducts (see Figure 1). The main objective of this study was to experimentally investigate the first-stage HTL of sweet sorghum bagasse to determine the product yields and their compositions under various severity conditions. The solids fraction from the first-stage HTL can be subsequently utilized in the second-stage HTL-HDO process to produce upgraded biocrude oil.²⁴

2. EXPERIMENTAL SECTION

2.1. Materials. The sweet sorghum bagasse was obtained from the Fort Valley State University experimental station (Fort Valley, GA, USA). Sweet sorghum variety of EJ7281 (Ceres Inc., Thousand Oaks, CA, USA) was squeezed to extract sugar juices. The remaining solids, sweet sorghum bagasse, was size-reduced with a knife mill into a fine powder with an average size of 0.3 mm and then oven-dried at 105 °C overnight. The sample was stored in a desiccator for subsequent use. Reagent-grade sulfuric acid was purchased from Sigma-Aldrich.

2.2. Biomass Characterization. The compositional characterization of the sweet sorghum bagasse was measured using both ultimate analysis and proximate analysis. The ultimate analysis was conducted with an elemental analyzer (LECO CHNS 932, LECO Corporation, St. Joseph, MI), based on the procedure of ASTM D3176-89, in which the oxygen content was obtained by difference.²⁵ The proximate analysis was conducted with a microthermogravimetric analyzer (Model TGA701, LECO Corporation, St. Joseph, MI), based

on the procedure of ASTM D5142-04 for coke, where the contents of ash, volatiles, and fixed carbon were reported on a dry basis.²⁶ The higher heating value (HHV) of sweet sorghum bagasse was analyzed with an adiabatic oxygen bomb calorimeter (IKAC 2000, IKA Works, Inc., Wilmington, NC, USA). The composition of structural carbohydrates and lignin was determined with the wet chemical analysis dictated by the National Renewable Energy Laboratory (NREL) standard protocol.²⁷

The lignin component was analyzed with pyro-GC-MS. About 2.0 mg of sample was pyrolyzed at 500 °C for 12 s with a Frontier lab pyrolyzer (PY-2020 iD). The volatile compounds were separated with a capillary column (30 m × 0.25 μm × 0.25 mm) (Model HP-5 ms, Agilent Technologies, Inc.), which combined with a 6890N GC system. The oven temperature program was initially set at 50 °C for 2 min and then ramped to 280 °C with the heating rate of 5 °C/min and kept constant for 7 min. Helium was employed as the carrier gas with a flow rate of 1 mL/min, and the split ratio was set at 50:1. The lignin components were identified with the aid of the NIST11 mass spectral library. Each experiment was repeated three times.

2.3. Design of First-Stage HTL Experiment. At the first-stage HTL, subcritical water at mild temperatures (160–200 °C) was applied to hydrolyze hemicellulose from sweet sorghum bagasse. The conditions for first-stage HTL were designed based on a severity factor ($\log R_0$), which was used to estimate the effects of reaction conditions and interpret polysaccharide degradation in thermal aqueous media.²⁸

$$R_0 = \int_0^t \exp\left(\frac{T(t) - T_{\text{ref}}}{14.75}\right) dt$$

where the temperature ($T/^\circ\text{C}$) is a function of time (t/min); T_{ref} represents the reference temperature ($T_{\text{ref}} = 100^\circ\text{C}$); 14.75 is an empirical parameter of activation energy, where the process kinetics were of first order and followed Arrhenius law.²⁹

Preliminary experiments at different severity levels were carried out to identify the range of conditions. Five different severity levels ranging from 3.4 to 4.0 were investigated for the optimal yield of C5 and C6 sugar mixtures. The experimental conditions for the first-stage HTL are described in Table 1.

Table 1. Experimental Conditions for the First-Stage HTL

temperature, T (°C)	time, t (min)	modified severity factor, $\log R_0$
160	60	3.55
160	90	3.73
170	30	3.55
170	45	3.72
170	60	3.85
170	90	4.02
180	15	3.56
180	20	3.68
180	30	3.85
180	45	4.02
190	10	3.69
190	15	3.86
200	2	3.43
200	5	3.73

2.4. First-Stage HTL Experiment. The first-stage HTL experiment was conducted using a Parr 5000 stainless steel, a multireactor with a heater and stirrer, and a process controller system (Parr Instrument Company, Moline, IL, USA). The maximum temperature and permissible pressure for the vessel are 300 °C and 3000 psi, respectively, with the vessel volume of 75 mL. A Teflon gasket was used to avoid pressured-gas leakage during reaction. The average heating rate was 10.2 °C/min, and the cooling rate in a water bath was 34.4 °C/min.

For each experiment, ~5.0 g of sweet sorghum bagasse powder was placed into the vessel, followed by the addition of 50 mL deionized (DI) water. The sample was well-mixed before loading. After measuring the total weight of the vessel and reactants, the reactor was assembly loaded and securely sealed. The air inside the vessel was purged and displaced with helium three times, and the headspace of the vessel was pressurized with high-purity helium to 300 psi. The suspension was continuously stirred at 300 rpm during the reaction. The first-stage HTL process was monitored through the Parr Specview Program. After the reaction, the vessel was removed from the heater system and immediately placed into a water bath vertically until reaching room temperature. The gas sample was then extracted from headspace through a Swagelok stainless-steel, blowdown needle valve into a sealed-air sample bag for gas chromatography–temperature-controlled desorption (GC-TCD) analysis. The vessel was then unloaded after releasing pressure through the blowdown valve. The liquid and solid products were weighed with the vessel and completely collected. An additional 25 mL DI of water was used to rinse the solid product to collect all residual materials.

hemicellulose, cellulose, or lignin conversion:

$$\text{conversion (\%)} = \left[1 - \left(\frac{\text{mass of hemicellulose, cellulose, or lignin in first-stage HTL solid product}}{\text{mass of hemicellulose, cellulose, or lignin in feedstock}} \right) \right] \times 100 \quad (1)$$

C5 or C6 sugar yield:

$$\text{sugar yield (\%)} = \left(\frac{\text{concentration of C5 or C6 sugar in first-stage HTL liquid product} \times \text{volume of liquid product}}{\text{mass of feedstock}} \right) \times 100 \quad (2)$$

C5 or C6 sugar recovery:

$$\begin{aligned} \text{sugar recovery} \\ &= \left(\frac{\text{mass of C5 or C6 sugar in first-stage HTL liquid product}}{\text{mass of hemicellulose or cellulose in biomass}} \right) \\ &\times 100 \end{aligned} \quad (3)$$

C5 or C6 sugar loss:

$$\begin{aligned} \text{sugar loss} = \\ \left(1 - \frac{\text{mass of C5 or C6 sugar in first-stage HTL liquid product}}{\text{converted C5 or C6 sugar}} \right) \times 100 \end{aligned} \quad (4)$$

Each experiment and analysis was repeated three times and the average value was reported. The product yields and C5 and C6 sugar conversions at various severity levels were plotted using Sigma Plot for Windows (ver. 12).

3. RESULTS AND DISCUSSION

3.1. Characterization of Sweet Sorghum Bagasse. The compositions and fuel properties of sweet sorghum bagasse are

The collected products were vacuum-filtered through Whatmann #4 90 mm filter paper. A post-acid treatment was implemented if necessary by adding an H₂SO₄ solution to the liquid product until a final concentration of 4% was reached and hydrolyzing at 121 °C for 1 h. The liquid samples were stored in a refrigerator before analysis, and solid samples were dried in an oven at 105 °C overnight and stored for the second-stage HTL experiment. Each experiment was repeated three times.

2.5. HTL Product Analysis. The collected gas sample from first-stage HTL was analyzed with GC-TCD using a Carboxen 1000 60/80 SS Packed column (15 ft × 1/8 in), which was specifically for H₂, O₂, N₂, CO, CH₄, and CO₂ identification. The inlet and detector temperatures were set at 100 and 140 °C, respectively. The temperature was initialized at 35 °C for 5 min and ramped up to 200 °C with the heating rate of 20 °C/min and held constant for 5.75 min. The gas sample injected was 50 μL, and helium was used as the carrier gas.

The liquid products of monosaccharides (xylose and glucose), carboxylic acids, and furan derivatives were analyzed with high-performance liquid chromatography (HPLC), using Coragel 94 column. The oven temperature was 60 °C, and 4 mM sulfuric acid was used for the mobile phase. The flow rate was constant at 0.6 mL/min. The sample volume injected was 5 μL.

For solid products, the elemental and biochemical compositions of structural carbohydrates and lignin, and lignin fractions were determined using ultimate analysis, wet chemical analysis, and pyro-GC/MS, respectively, as similar to the procedures described above for sweet sorghum bagasse.

The calculations of products conversion were defined as follows:

given in Table 2. After juice extraction, the residual soluble sugars in the bagasse accounted for 11.55 wt %, in which glucose accounted for 49.4%, sucrose 16.1%, and fructose 34.6%. The residual soluble saccharides were widely reported as the majority of extracted juice in the range from 43% to 58%.³⁰ However, minor saccharides in juice such as xylose, galactose, arabinose, and mannose were not detected from sweet sorghum bagasse as the availability of these minor saccharides varies significantly with genetic, climatic, and edaphic factors.³⁰ The lignin occupied 17.66 wt % of the total biomass; most lignin was formed from *p*-hydroxyl phenol (H lignin) units. The proportions of hemicellulose and cellulose were 19.68 and 36.17 wt %, respectively, in the sweet sorghum bagasse. The compositional characterization was comparable to other sweet sorghum bagasse in open literature.^{31,32} A higher ash content was observed due to the accumulation of alkaline metal oxides from different plantation conditions, soil types, and cultivars.³⁰ The H/C and O/C ratios were 1.57 and 0.94, respectively, and they were similar to that of whole sorghum.³³ These ratios indicated an undesirable energy density of raw sweet sorghum bagasse with an HHV of 16.30 MJ/kg, which is much less than that of biocrude oil at 32–36 MJ/kg.³⁴

Table 2. Compositional Analysis of Sweet Sorghum Bagasse Sample^a

component	amount
Ultimate Analysis	
C (%), dry)	41.30 (0.11)
H (%), dry)	5.39 (0.04)
N (%), dry)	1.32 (0.14)
O (%), dry)	51.98 (0.21)
O/C	0.94
H/C	1.57
Proximate Analysis	
moisture (wt %)	7.36 (0.03)
volatile carbon (%), dry)	77.03 (0.12)
fixed carbon (%), dry)	18.38 (0.12)
ash (%), dry)	4.59 (0.03)
soluble ash (%), dry)	66.2
insoluble ash (%), dry)	33.8
Higher Heating Value (MJ/kg)	16.30 (0.25)
Carbohydrates and Lignin Compositions Analysis	
lignin (wt %)	17.66 (2.38)
syringyl (wt %)	9.54 (1.97)
guaiacyl (wt %)	34.58 (2.03)
p-hydroxyl phenol (wt %)	55.97 (1.04)
hemicellulose (wt %)	19.68 (0.36)
cellulose (wt %)	36.17 (0.63)
soluble residue sugars (wt %)	11.55 (2.72)
sucrose (wt %)	16.05
glucose (wt %)	49.37
fructose (wt %)	34.58

^aThe numbers shown in the parentheses represent the standard deviations with $n = 3$.

3.2. Analyses of First-Stage HTL Products. **3.2.1. Yields of First-Stage HTL Products.** The severity factor was specially developed for explaining and predicting the hydrolysis of xylan and cellulose in the hydrothermal process.³⁵ Under the

designed conditions of first-stage HTL in Table 1, the product yields were summarized in Table 3.

The yields of solid and liquid products were relatively stable at ~44% and ~55%, respectively; the exceptions occurred when gas products were generated. Gas products were only detected at higher temperatures (>190 °C) or with higher severity factors (>3.85), which indicated that gas was a secondary product from holocellulose-decomposed intermediates. CO₂ was the only identified component in the gas product, which mainly accumulated due to decarboxylation reaction of xylose and the products of acetic acid and formic acid.³³ When the reaction severity factor was >3.85 , decomposition reactions of secondary intermediates, such as sugars and their derivates, started to control the kinetics of HTL process and impacted the hydrolyzed products.

3.2.2. Composition of the Solids Fraction. The majority of solid fraction after first-stage HTL consisted of hemicellulose, cellulose, and lignin (see Table 4). Compared to hemicellulose content, the variations of cellulose and lignin contents in the solids fraction were relatively stable at different severity factors. The remaining hemicellulose showed a decreasing trend with the increase of reaction severity. In addition, it was observed that a combination of lower temperature and longer holding time was more desirable for removing hemicellulose in solid fraction except under the conditions of 200 °C for 5 min at log $R_0 = 3.70$. It was consistent with Garrote et al.'s study that the reaction temperature significantly affected the hydrolysis kinetics of hemicellulose.¹⁴

The lignin fractions of the solid product were analyzed using a pyro-GC/MS, as shown in Figure 2. p-Hydroxyphenyl (H), guaiacyl (G), and syringyl (S) were phenylpropanoids lignin units produced from the following three lignin monolignols: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, respectively.³⁶ It was reported that wood lignin mainly consisted of G unit, whereas grass lignin contained comparable G and S units, with more H lignin than hardwood.³⁷ After first-stage HTL, there was no significant difference among G, S and H lignin contents. However, with an increase in temperature, a

Table 3. Yields of First-Stage HTL Products

modified severity factor (log R_0)	temperature, T (°C)	time, t (min)	Yield ^a (wt %)		
			gas	solid	aqueous
3.40 ± 0.3	200	2	4.04 (1.31)	44.85 (5.41)	51.11 (6.72)
3.55 ± 0.3	160	60	0.00 (0.00)	46.33 (2.00)	53.67 (2.00)
	170	30	0.00 (0.00)	41.33 (2.67)	58.67 (2.67)
	180	15	0.00 (0.00)	45.00 (2.17)	55.00 (2.17)
3.70 ± 0.3	160	90	0.00 (0.00)	41.67 (2.00)	58.33 (2.00)
	170	45	0.00 (0.00)	43.33 (3.67)	56.67 (3.67)
	180	20	0.00 (0.00)	42.83 (2.25)	57.17 (2.25)
	190	10	4.04 (0.35)	45.25 (2.37)	50.71 (2.02)
	200	5	4.04 (1.31)	48.08 (3.79)	47.88 (5.11)
3.85 ± 0.3	170	60	3.33 (0.00)	43.33 (0.67)	53.33 (0.67)
	180	30	3.33 (0.00)	39.00 (1.83)	57.67 (1.83)
	190	15	3.33 (0.00)	41.33 (1.67)	55.33 (1.67)
4.00 ± 0.3	170	90	3.33 (0.00)	43.00 (2.17)	53.67 (2.17)
	180	45	6.67 (1.67)	36.33 (3.50)	57.00 (5.17)

^aThe numbers shown in the parentheses represent the standard deviations with $n = 3$.

Table 4. Composition of First-Stage HTL Solid Products

modified severity factor ($\log R_0$)	temperature, T (°C)	time, t (min)	Lignin and Structural Carbohydrates in First-Stage HTL Solid Products ^a (wt %)			
			lignin	hemicellulose	cellulose	residues (wt %)
3.40 ± 0.3	200	2	37.12 (1.80)	8.09 (0.02)	55.60 (2.12)	3.46
3.55 ± 0.3	160	60	32.60 (2.57)	12.34 (0.89)	51.41 (0.12)	3.35
	170	30	36.40 (1.35)	12.69 (0.09)	52.23 (0.93)	3.75
	180	15	35.71 (3.58)	13.51 (0.53)	58.03 (0.14)	3.45
3.70 ± 0.3	160	90	34.79 (2.24)	11.45 (0.03)	52.12 (1.80)	3.72
	170	45	34.64 (3.08)	10.61 (0.11)	45.37 (0.70)	3.58
	180	20	36.63 (1.63)	12.23 (0.86)	56.76 (4.79)	3.62
	190	10	36.12 (0.78)	8.40 (0.60)	53.07 (5.41)	3.43
	200	5	34.71 (3.39)	2.36 (0.13)	45.40 (0.19)	3.23
3.85 ± 0.3	170	60	34.69 (3.16)	4.99 (0.05)	41.67 (0.38)	3.58
	180	30	38.13 (1.82)	6.45 (0.20)	51.73 (2.52)	3.98
	190	15	38.64 (2.28)	6.35 (0.22)	55.29 (2.91)	3.75
4.00 ± 0.3	170	90	33.14 (3.13)	2.74 (0.03)	42.70 (2.18)	3.61
	180	45	39.58 (3.56)	5.03 (0.12)	48.57 (2.59)	4.27

^aThe numbers shown in the parentheses represent standard deviations with $n = 3$.

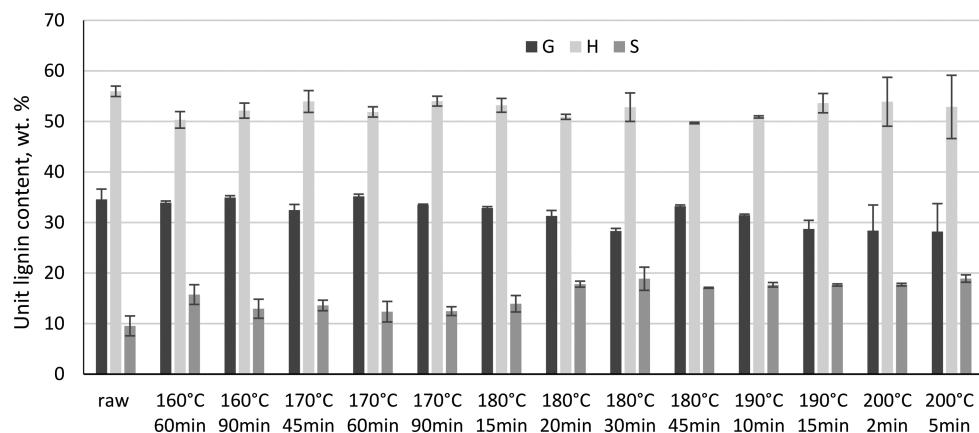


Figure 2. Lignin components of first-stage HTL solid products.

slight decline in G lignin content, as well as a slight increase in S lignin content was observed.

3.2.3. Hydrolysis of Hemicellulose, Cellulose, and Lignin.

The conversion of hemicellulose, cellulose, and lignin after first-stage HTL under various severity conditions is shown in Figure 3. Most hemicellulose was hydrolyzed under the designed HTL conditions, followed by cellulose and a small amount of lignin. The original hemicellulose content of sweet sorghum bagasse was 19.68%, and the highest hemicellulose conversion of 95.2% occurred at 200 °C for 5 min, followed by 94.1% at 170 °C for 90 min. It was also found that, within the first several minutes of the reaction, a large amount of hemicellulose was hydrolyzed. The hemicellulose hydrolysis rate remarkably decreased over time until reaching a balance, at which point the hydrolysis rate of hemicellulose equaled the degradation rate of monomer xylose. We proposed that, rather than having an inhibitive effect on the decomposed products, fast hydrolysis of hemicellulose occurred simultaneously with slow hydrolysis at lower temperatures. A fraction of hemicellulose, which was less tolerant to temperature, could be more rapidly and directly hydrolyzed into xylose rather than through oligomer xylose; the remaining

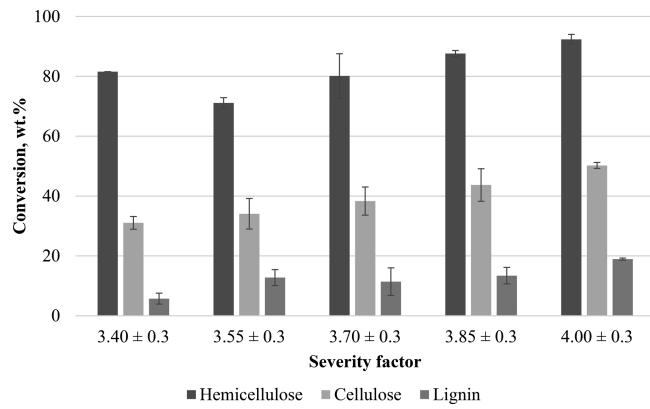


Figure 3. Percent conversion of hemicellulose and cellulose in sweet sorghum bagasse under various first-stage HTL severity conditions.

hemicellulose was supposed to be more stable and gradually hydrolyzed into oligomer xylose with much lower reaction constant. The observed result on hemicellulose hydrolysis was in accordance with Shen's kinetics model.⁹

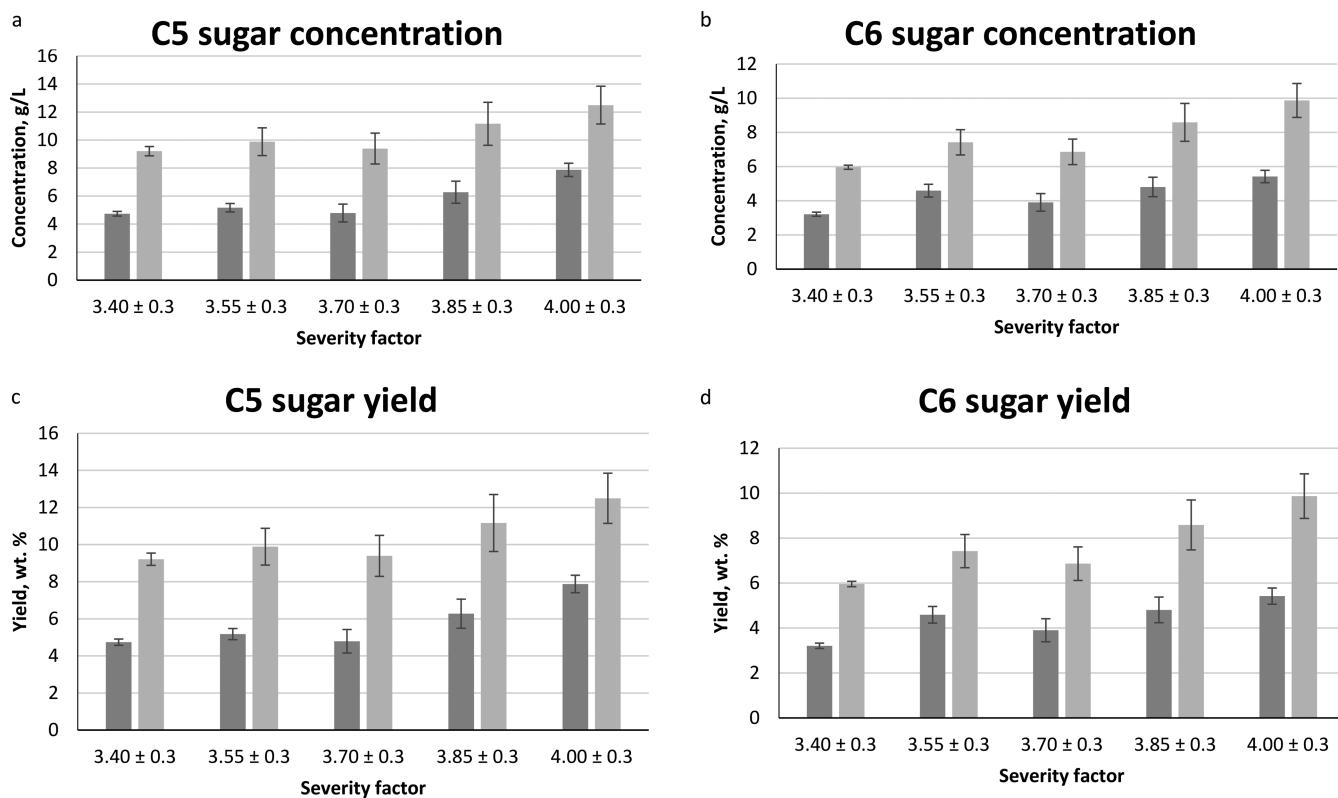


Figure 4. C5 and C6 sugar concentrations and yields from sweet sorghum biomass under various first-stage HTL severity conditions.

In addition to hemicellulose hydrolysis, a fraction of cellulose, especially amorphous cellulose was simultaneously hydrolyzed into C6 oligomer and monomer sugars. At each designated reaction temperature, the cellulose content of the solid product decreased over time. However, the maximum hydrolysis of cellulose stopped at ~50%, where almost all of the amorphous cellulose was completely hydrolyzed. For instance, at the severity factor of 3.85, 170 °C for 60 min could be enough to accomplish all the amorphous cellulose hydrolysis, while 88% amorphous cellulose was converted at 180 °C for 30 min and 74% at 190 °C for 15 min (see the *Supporting Information*).

Although most lignin fractions are thermally resistant until ~400 °C, a small fraction of lignin had low thermal tolerance and decomposed during the first-stage HTL through the breakage of lignin–carbohydrate bonds and depolymerization reactions.³⁸ It was found that ~10%–15% of lignin was degraded below 200 °C and slight variations were observed with the change of severity factors. Our result was consistent with Yang's study on pyrolysis,³⁹ but the decomposed temperature of lignin was less than that of Wittkowski's study at 230 °C.⁴⁰ It was observed that the high ionic product of subcritical water favored the radical reactions to improve the scissions of oxygen functional groups from lignin structure and, therefore, displayed different thermal stabilities under HTL conditions.⁴¹ However, no lignin degraded compounds, such as phenolics or benzenediols, were detected in this study.

3.2.4. Analysis of C5 and C6 Sugar Mixtures. Xylose was the most found compound in liquid product after HTL, followed by glucose and arabinose. Fructose, sucrose, and mannose were also detected, but at concentrations too low to be reliably quantified. Therefore, the analyzed C5 sugars were the summary of xylose and arabinose from hemicellulose

hydrolysis. As similar to cellulose, part of the hemicellulose was hydrolyzed in the form of monosaccharides; however, another fraction existed as oligomers that were not easily detectable. Therefore, post-acid treatment was employed as a depolymerization step of C5 and C6 oligosaccharides into monomers, typically for C5 sugars from hemicellulose hydrolysis, as hemicellulose was composed of branched heteropolymers of various monosaccharides. The maximum concentrations of C5 and C6 sugar were initially at 9.57 g/L and 6.93 g/L in HTL liquid product, respectively. The maximum concentrations increased ~78% after post-acid treatment (see Figures 4a and 4b). In contrast to Shen's study, our results had ~10 times enhancement on the yields of glucose and xylose after post-acid treatment.⁹ We found that the monomer sugars yields increased moderately, ranging from 45% to 70%, because of the different structural components and tolerance levels of holocellulose in sweet sorghum bagasse, compared to that of corn stover.⁹ More importantly, the higher ionic product of subcritical water favored ionic reactions.⁴² This study further demonstrated the advantage of subcritical water as a solvent during HTL hydrolysis of hemicellulose and cellulose, which promoted the depolymerization process and could reduce acid use in subsequent treatment. After post-acid treatment, the maximum concentrations of C5 sugars and glucose were 17.04 g/L at 170 °C for 60 min and 12.32 g/L at 170 °C for 90 min, respectively. The optimal HTL condition for producing C5 and C6 sugars was 170 °C for 60 min with a total sugar concentration of 28.52 g/L in liquid product.

The C5 and C6 sugar yields were calculated from their respective concentrations and described in Figure 4. Although the highest hemicellulose conversion occurred at 200 °C for 5 min, the C5 sugar yield under this condition was as low as 1.72%. Most hemicellulose hydrolysis products at this temper-

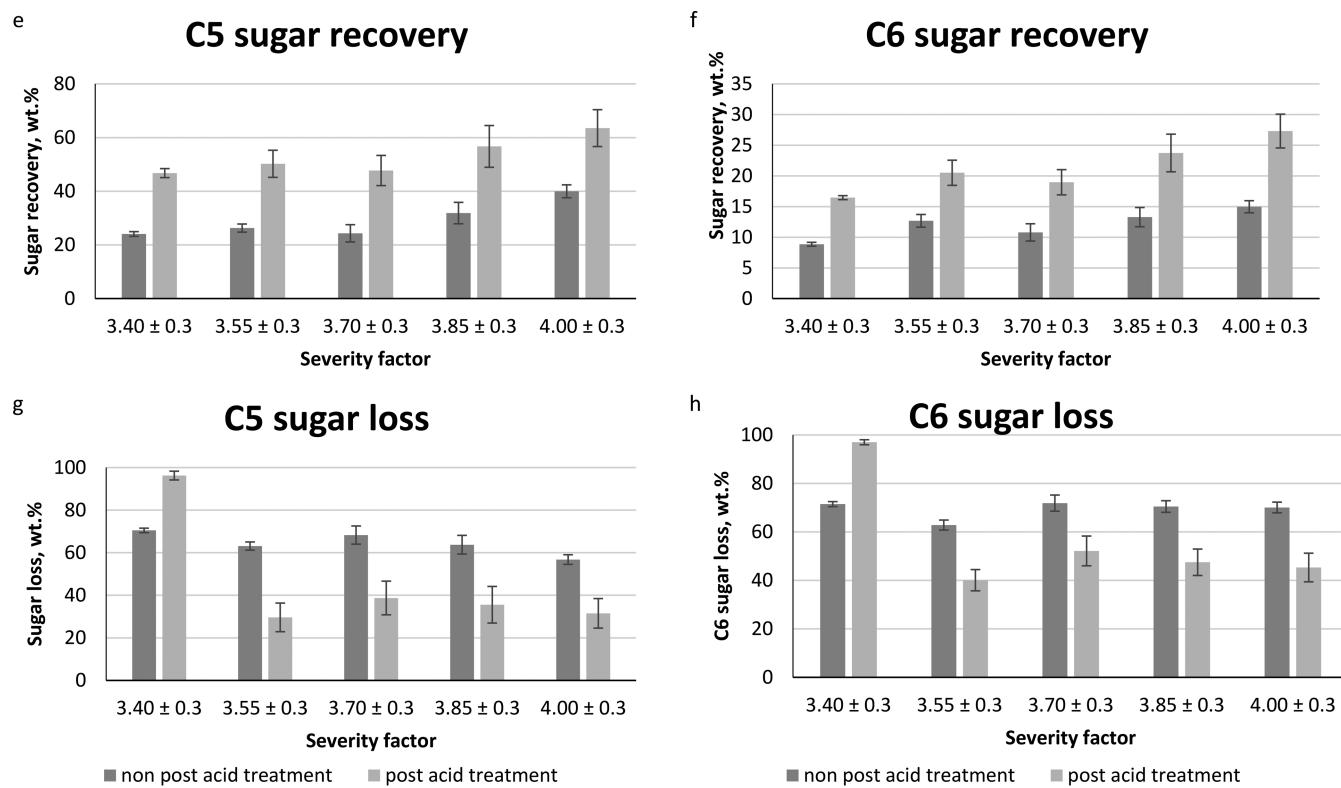


Figure 5. C5 and C6 sugar loss and recovery from sweet sorghum biomass under various first-stage HTL severity conditions.

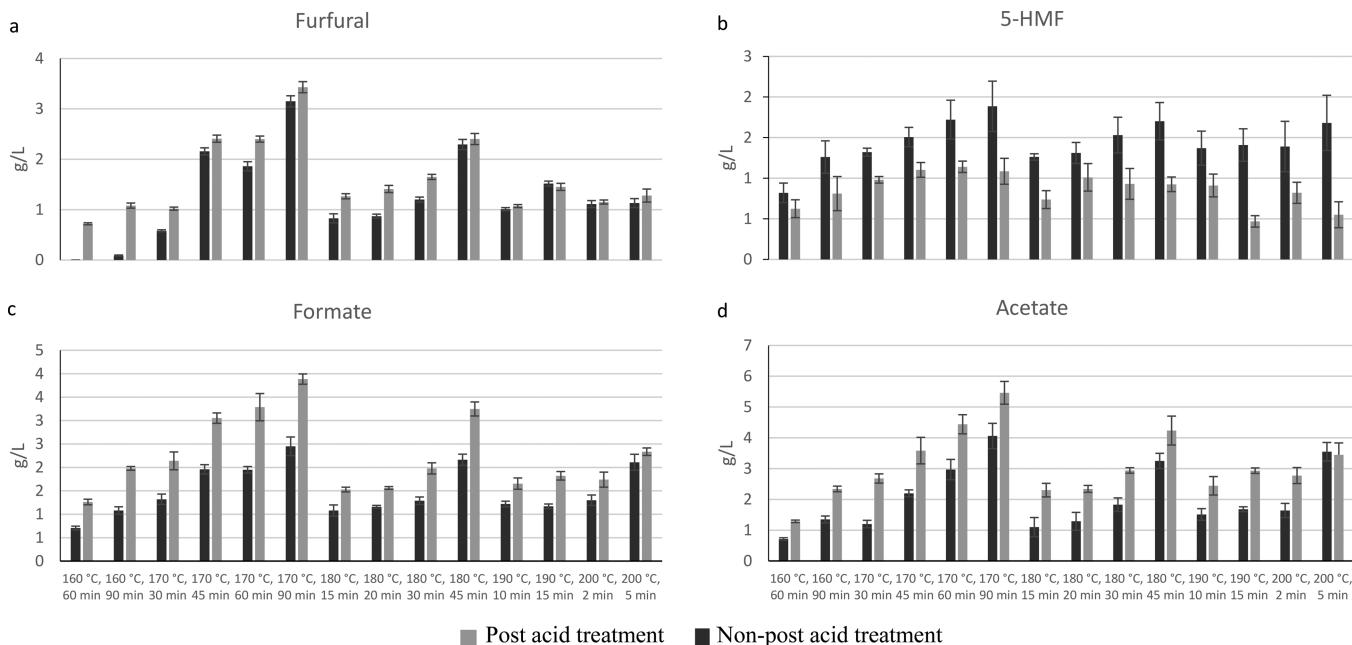


Figure 6. Yields of other compounds in the first-stage HTL liquid product.

ture were further decomposed to furfural, acetate, and formate (see Figure 6, presented later in this work). Actually, when the reaction temperature reached 180 °C, the C5 sugar yield was reduced dramatically (see Figure 4c), resulting from the decomposition of C5 sugar into furan derivatives and carboxylic acids. The maximum C5 sugar yield of 17.04% was obtained at 170 °C for 60 min with post-acid treatment. Although the hemicellulose continued to decompose after 60 min, less C5 sugar yield was observed. This phenomenon was due to the

degradation rate of C5 sugar to furfural being higher than the rate of C5 sugar yield from hemicellulose. C5 and C6 sugar recoveries also had similar trends of yields, because, at higher reaction severities, typically, the reaction temperatures promoted the conversion rates of furfural and 5-hydroxymethylfurfural (5-HMF) from sugars. However, considering the residual hemicellulose in solid product, the condition of 170 °C for 90 min was more appropriate and should be employed for

first-stage HTL, in which 94% of hemicellulose was hydrolyzed, with a sugar mixture recovery of 94.1%.

The sugar decomposition kinetics and hemicellulose hydrolysis process collectively impacted the sugar loss. Figure 5 shows that the largest sugar loss occurred at the lowest severity factor of 3.4, which caused the lowest yields of C5 and C6 sugars from biomass. C5 sugars showed more mass loss than C6 sugars at a higher HTL severity factor of 4.0 (180 °C for 45 min). It was proposed that, when the converted sugar amount was given, C5 sugars were less thermally stable than that of glucose, because of the dehydration kinetics of xylose into furfurals, which was more sensitive, relative to the severity factor. The percent sugar yield, recovery, and loss from first-stage HTL are summarized in the *Supporting Information*.

3.2.5. Analysis of Other Compounds in Liquid Products. The yields of other dominant aqueous components in the liquid product were also analyzed using HPLC and are shown in Figure 6. The yields of 5-HMF, furfural, acetate, and formate increased with holding time, showing similar trends as C5 and C6 sugars. 5-HMF and furfurals are unstable intermediates from the dehydration of glucose and xylose and could further degrade into carboxylic acids, typically formic acid and acetic acid, through ring scissoring and oxidation.⁴³ The maximum yields for 5-HMF (3.43 g/L), furfural (1.89 g/L), acetate (3.89 g/L), and formate (5.46 g/L) were obtained at 170 °C for 90 min. It was also observed that a post-acid hydrolysis treatment produced more furfural and carboxylic acids, except 5-HMF. Yin reported that 5-HMF was degraded to formate and 1,2,4-benzenetriol under acidic conditions, causing increased carboxylic acid concentration.⁴⁴ However, 1,2,4-benzenetriol were neither detected with GC-MS nor HPLC. It can be deduced that other unidentified pathways might involve 5-HMF degradation. Under the above concentrations of furans and carboxylic acids, *S. cerevisiae*, which is an industrial yeast strain to ferment ethanol from C5 and C6 sugars, was reported to be adaptable and active.⁴⁵ Therefore, the first-stage HTL sugar streams can be a suitable feedstock for bioethanol fermentation or producing other biochemicals or bioplastics.

4. CONCLUSIONS

A two-stage hydrothermal liquefaction (HTL) process was developed for sweet sorghum bagasse. In the first-stage HTL study, a lignin-rich solids fraction was prepared for producing high-quality biocrude oil with the coproduct of sugar-rich mixtures. It was optimized that 170 °C for 60 min was effective in hydrolyzing 94.1% of hemicellulose and 49.2% of cellulose to produce maximum sugar yield of 28.14% with the concentration of 28.52 g/L after post-acid treatment. In addition, ~58% carbon in the sweet sorghum bagasse was converted to C5 and C6 sugars during the first-stage HTL. The C5 and C6 sugar mixtures with a small amount of 5-HMF, furfural, and carboxylic acids can be directly used or blended with sweet sorghum juices to ferment bioethanol or value-added chemicals. The lignin-rich solid product, containing ~33.1 wt % lignin, 42.7 wt % cellulose, 2.7 wt % hemicellulose, and 3.6 wt % water-insoluble ash, could be further converted in the second-stage HTL-HDO process to produce upgraded biocrude oil.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.energyfuels.8b00668](https://doi.org/10.1021/acs.energyfuels.8b00668).

Conversion of hemicellulose, cellulose, and lignin from sweet sorghum bagasse under various first-stage HTL conditions (Table S1), and sugar yield, recovery, and loss from sweet sorghum biomass under various first-stage HTL conditions (Table S2) ([PDF](#))

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Notes

The authors declare no competing financial interest.

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