

# Two-Stage Hydrothermal Liquefaction of Sweet Sorghum Biomass—Part II: Production of Upgraded Biocrude Oil

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## Supporting Information

**ABSTRACT:** The hydrothermal liquefaction (HTL), followed by hydrodeoxygenation (HDO) of lignin-rich biomass has a potential to improve the yield and the quality of upgraded biocrude oil. In this study, the lignin-rich biomass obtained from the low-temperature HTL (stage 1) of sweet sorghum bagasse was investigated to evaluate the biocrude oil yield and its compositions using catalytic high-temperature HTL-HDO (stage 2) and was compared with the conventional, whole-stage HTL-HDO process. Biocrude oil yield was achieved up to 38% during a high-temperature HTL, while 42% was obtained after catalytic (5% Ru/C) HDO process. Up to 96% hydrocarbon content of biocrude oil was achieved, which is twice as high as that of the conventional whole-stage HTL-HDO process. Aromatic hydrocarbons and long-chain alkanes were also dominant in the upgraded biocrude oil, which collectively accounted for 28% of the total hydrocarbons. From raw sweet sorghum bagasse, the hydrocarbons yield from second-stage HTL-HDO process (11%) was substantially increased by 78%, compared to that of the whole-stage HTL-HDO process (7%). The upgraded biocrude oil could be directly processed or co-processed in the existing refinery to produce drop-in fuels.

## 1. INTRODUCTION

Lignocellulosic biomass is both sustainable and renewable energy resources for biofuel production, because of its abundant availability and potential to reduce greenhouse gas emissions. Sweet sorghum, which is a typical C4 annual energy crop, can be grown on uncompetitive arable land. This energy crop has a short growth cycle, produces high biomass yield, requires low fertilization input, and is tolerance to drought conditions.<sup>1–3</sup> Therefore, it can be an excellent biorefinery feedstock to produce a diverse stream of biochemical and biofuels. Sweet sorghum biomass also accumulates sugars in plant stalks, which can be squeezed to extract juices rich in sucrose.<sup>4,5</sup> The sugar content of the juice varies from 9% to 15%, with the total juice yield of 3.6–15.5 Mg ha<sup>−1</sup>. The bagasse, which is the byproduct of stalk after juice extraction, represents approximately two-thirds of the dry biomass, and has limited value, because of its low energy content and high stalk moisture content.<sup>6</sup> However, the bagasse with high moisture content ranging from 60% to 80% (wet basis) could be an excellent feedstock for hydrothermal liquefaction (HTL)-based biorefinery.

Hydrothermal liquefaction (HTL) is a rapidly developing technology to convert wet biomass into biocrude oil using subcritical water as the solvent at moderate temperature (280–370 °C) and high pressure (10–25 M Pa).<sup>7</sup> During the HTL process, all the solid biomass is completely dissolved into mainly liquid and gaseous products. The liquid product can be further separated into aqueous and oil (biocrude oil) fractions. The unconverted solids and other inorganic minerals in the biomass are called residual solids or char. The HTL biocrude oil yield from lignocellulosic biomass ranged from 30% to 40%;<sup>8–12</sup> this yield was impacted by various HTL parameters, including temperature, catalyst, and retention time. It was reported that the typical HTL temperature range was from 300

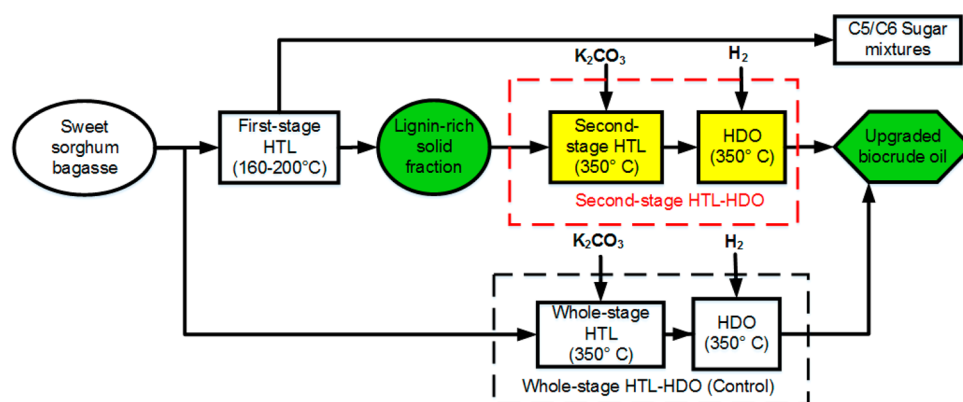
°C to 350 °C, to obtain a maximum biocrude oil yield using water as a solvent with or without catalysts.<sup>13–16</sup> The utilization of an alkaline catalyst in the HTL process suppresses the formation of solid products, which would enhance the biocrude oil yield.<sup>9</sup> Karagöze et al. employed 0.94 M K<sub>2</sub>CO<sub>3</sub> as a catalyst to HTL of wood and found that the biocrude oil yield increased from 17.8% to 33.7%, and the solid residue yield was reduced from 42% to 4%.<sup>17,18</sup> For most lignocellulosic biomass, the reported optimum holding time ranged from 15 min to 60 min, depending on the reaction temperature (250–375 °C) and heating rate (5–140 °C/min).<sup>7,19,20</sup> Alkaline catalyst improved the processes of hydrolysis and decomposition and shortened holding time; however, the most important effect of alkaline catalyst was to increase biocrude oil yield.<sup>21</sup> It was also reported by Boocock<sup>22</sup> and Zhu<sup>13</sup> that the prolonged holding time suppressed the biocrude oil yield, because the cracking reaction of biocrude oil or its precursors promoted the formation of gases and chars through condensation and repolymerization reactions.<sup>23</sup> The reduction in oil yield with longer holding time was also confirmed by the National Collaborative Research Infrastructure Strategy (NCRIS, University of Sydney, Australia) through a continuous HTL process, which reported that shorter residence time with a higher heating rate benefited the higher biocrude oil yield.<sup>24</sup>

The obtained biocrude oil through HTL contains a wide range of highly oxygenated small molecular compounds as well as undesirable water, which resulted in poor combustion properties, because of low heating value, high acidity, high reactivity, and corrosion against combustor.<sup>25</sup> Therefore, hydrodeoxygenation (HDO) is essentially required to improve

Received: March 8, 2018

Revised: May 11, 2018

Published: May 15, 2018



**Figure 1.** Schematic of the two-stage HTL-HDO process for sweet sorghum biomass to produce upgraded biocrude oil.

biocrude oil quality by catalytically removing oxygenated compounds from biocrude oil through HDO and decarboxylation reactions in the presence of hydrogen and heterologous catalysts at moderate temperature (250–450 °C) and high pressure (75–300 bar) before applying for drop-in fuels.<sup>26</sup> The most commonly used HDO catalyst is ruthenium metal catalyst supported with carbon (Ru/C), which has high potential to increase biocrude oil yield (52%) and higher degree of HDO (86%) among various transition-metal catalysts at 350 °C for a reaction time of 4 h.<sup>27,28</sup>

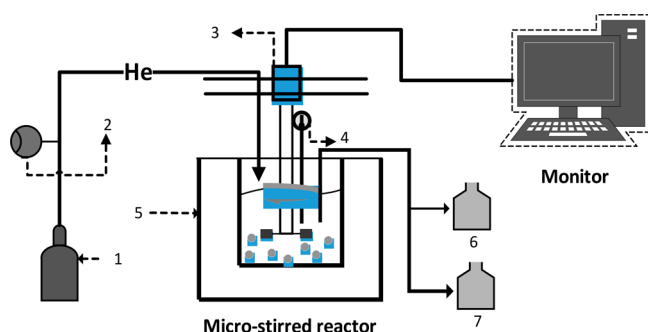
One major issue concerning HTL of lignocellulosic biomass is that the presence of hemicellulose in the biomass limits the biocrude oil yield and further impairs the downstream HDO upgrading process, because of the high content of relatively small oxygenates.<sup>29</sup> Although the hemicellulose in the biomass accounts for ~20%–40%, it was reported to contribute only up to 5.3% of biocrude oil yield.<sup>30</sup> The majority of the hemicellulose during the HTL process were converted to aqueous compounds (up to 42%).<sup>30</sup> Liu also reported that cross reactions occurred between hemicellulose-derived intermediates and lignin units, which further promoted the formation of solid residues through repolymerization reactions.<sup>31</sup> However, limited research was conducted on improving the HTL oil yield, while effectively utilizing all fractions of the lignocellulosic biomass into useful products. Therefore, we developed a two-stage HTL-HDO technology to comprehensively utilize lignocellulosic biomass. In the first-stage HTL, hemicellulose in the biomass can be selectively hydrolyzed under low-temperature HTL conditions and the remaining lignin-rich solid are prepared for further conversion to upgraded biocrude oil (see Figure 1). The optimal first-stage HTL conditions for sweet sorghum bagasse and the sugar yields were investigated in our previous study and found that (i) ~94.1% of hemicellulose and 49.2% cellulose were respectively hydrolyzed to C5 and C6 sugars platform with a concentration of 28.52 g/L; (ii) the coproduct of lignin-rich solid fractions, which represents an ideal source of phenolics feedstock, can be further hydrothermally liquefied to form high-quality biocrude oil.<sup>32</sup> This article aims to investigate the feasibility of conversion pretreated lignin-rich biomass into high-quality biocrude oil. The main objectives of this paper were to experimentally investigate the high-temperature HTL-HDO of lignin-rich sweet sorghum bagasse to determine the biocrude oil yield, compared with the whole-stage HTL-HDO process and to evaluate the fuel characteristics and the compositions of second-stage HTL and HDO upgraded biocrude oil to produce drop-in biofuels.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Sweet sorghum bagasse used for the whole-stage HTL-HDO was obtained from the experimental research station in Fort Valley State University, Fort Valley, GA, USA. One variety of sweet sorghum (EJ7281, Ceres, Inc., Thousand Oaks, CA) was harvested in mid-October, and the stalks were squeezed to extract sugar juices. With regard to the remaining solids, sweet sorghum bagasse was reduced in size, using a knife cutting mill (Model SM 2000, Retsch, Germany), to form 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. It was composed of ~20% hemicellulose, 36% cellulose, and 18% lignin. The lignin-rich sweet sorghum bagasse used in the second-stage HTL-HDO was prepared from the first-stage HTL process, using the optimal conditions of 170 °C for 90 min, based on our previous study.<sup>32</sup> The lignin-rich biomass contained ~33% lignin and 43% cellulose with a negligible hemicellulose content. Reagent-grade dichloromethane (DCM), magnesium perchlorate, and 5% ruthenium on carbon (Ru/C, particle size of 20 μm) were all purchased from Sigma–Aldrich.

**2.2. HTL and HDO Experiment.** The stainless-steel reactor utilized for HTL and HDO was a system of batch microstirred reactors (Model Parr 4598, Parr Instrument Company, Moline, IL, USA) with a maximum temperature of 500 °C and pressure of 5000 psi. The vessel capability was 100 mL. A consumable Parr Grafoil graphite gasket was used to avoid pressurized gas leakage during reaction. A four-blade impeller (0.81 in diameter) powered by a magnetic stirrer (Parr Instruments, Model No. A1120HC6, 1/8 hp variable speed) provided agitation with a maximum speed of 750 rpm. The vessel was heated through a ceramic fiber external jacket (700 W), and the processes of HTL and HDO reaction were monitored with Parr Specview Software. The sketch of the experimental apparatus is shown in Figure 2. The average heating rate was 14 °C/min; the average cooling rate was 34.5 °C/min in a water bath.

About 5.0 g of dried sweet sorghum bagasse sample was placed into the vessel, followed by the addition of 50 mL of 0.94 M potassium carbonate solution or water for each HTL and control experiment. Helium was used to purge and displace the air in headspace until 500 psi was reached. The reaction was monitored through Parr Specview Software at a temperature of 350 °C and with an agitation of 300 rpm. After the holding time, the vessel was immediately cooled in a water bath until reaching room temperature. The gas sample was then collected from the headspace through a blowdown needle valve into a sealed-air sample bag. The vessel was unloaded after releasing pressure through the blowdown valve. The liquid and solid products were analyzed or immediately used for the HDO experiment. Based on the previous studies,<sup>33–35</sup> homogeneous alkaline catalyst, K<sub>2</sub>CO<sub>3</sub> was used as a catalyst in the present study; and three different holding times (15, 30, and 60 min) were investigated for the whole-stage HTL to study the effects on biocrude oil yield and its quality. The optimum condition of the whole-stage HTL process for the maximum biocrude oil yield was used to study the second-stage HTL. In the second-stage



**Figure 2.** Schematic graph of an experimental microstirred reactor. [Legend: 1, helium cylinder; 2, pressure gauge; 3, rotor; 4, thermocouple; 5, heating jacket; 6, gas sample collector; and 7, liquid sample collector.]

HTL, the lignin-rich sweet sorghum bagasse obtained from first-stage HTL conditions (170 °C for 90 min) was used to determine the biocrude oil yield and its compositions.

**HDO Experiment.** The hydrodeoxygenation (HDO) experiment was carried out immediately after HTL experiment in the same Parr reactor. Approximately 1.5 g Ru/C was added as a catalyst into the vessel. The properties of the Ru/C catalyst have been reported in our previous study with a surface area of 714 m<sup>2</sup>/g, an average pore size of 14.4 Å, and a pore volume of 0.52 cm<sup>3</sup>/g.<sup>36</sup> Hydrogen was used to purge the headspace under a pressure of 50 psi for 30 s three times and finally pressurized until 500 psi was reached. The HDO process was conducted at 350 °C for 4 h with an agitation rate of 500 rpm. After HDO reaction, the gas sample was collected in a manner similar to that used for the HTL procedure described previously. After unloading the vessel, the solid and liquid samples were collected and stored in a refrigerator at 4 °C before separation for compositional analysis. Three replicates of HTL and HDO operations were carried out and the average data was reported with standard derivation. All the yields and compositions of HTL products were determined based on a mass basis.

**2.3. Separation and Extraction Procedures.** Approximately 40 mL of DCM solvent was added into the mixture of HTL or HTL-HDO liquid and solid products to extract biocrude oil (oil phase). The mixture was then filtered with vacuum filtration through Whatmann No. 4 90 mm filter paper. The solid residue was rinsed with an additional 15 mL of DCM to collect residual biocrude oil. The rinsing solution was merged with the filtrate. The biocrude oil fraction in liquid products was extracted with the combined DCM and decanted off from the aqueous phase using a separatory funnel. To remove residual moisture, 1.0 g of anhydrous (magnesium perchlorate) was added into the biocrude oil fraction. This anhydrous-biocrude oil mixture was then filtered again through Whatmann No. 4 90 mm filter paper, and the extracted dewatered biocrude oil fraction was further transferred to a round-bottomed flask for rotary evaporation in a water

bath of 36 °C for 60 min under a vacuum of 2 mmHg. The DCM free biocrude oil or upgraded biocrude oil was then collected and weighed before storage in a refrigerator for compositional analysis.

**2.4. HTL and HDO Products Analysis.** Major compounds in aqueous products were determined with HPLC using a Coragel 94 column with the mobile phase of 4 mM sulfuric acid at the flow rate of 0.6 mL/min. The oven temperature was kept constantly at 60 °C. A 5 μL sample was injected for analysis.

The elemental composition of biocrude oil was measured using an elemental analyzer (Model LECO CHNS 932, LECO Corporation, St. Joseph, MI), based on the procedure of ASTM Standard D3176-89, in which oxygen content was obtained by difference.<sup>37</sup> The moisture content of biocrude oil was measured with Karl Fisher Titration.<sup>38</sup>

The higher heating value (HHV) of biocrude oil could be calculated based on the elemental composition, using the Dulong Formula, which can be described as<sup>39</sup>

$$\text{HHV (MJ/kg)} = 0.3383C + 1.422\left(H - \frac{O}{8}\right)$$

The compositions of biocrude oil were analyzed with gas chromatography–mass spectroscopy (GC-MS), using a HP-5 ms capillary column (30 m × 0.25 μm × 0.25 mm). The GC oven temperature was set to 40 °C initially and held for 4 min, then ramped at 5 °C/min until 275 °C and held consistently for 5 min. The Mass Spec interface and inlet temperature were set at 280 and 260 °C, respectively. Helium was employed as GC carrier gas at the flow rate of 0.8 mL/min. The split ratio was set to 50:1. The electron impact (EI) ionization was set at 70 eV with a mass-to-charge range from 50 μ to 600 μ. Major compounds identified with GC-MS from biocrude oil and upgraded biocrude oil were quantitatively analyzed with an internal standard method. Neat compounds of toluene, trimethylbenzene, pentadecane, 2-methoxy phenol, and 2-cyclopenten-1-one were used to estimate the mass percentage of aromatic hydrocarbons, benzenes, alkanes, phenols, and cyclic ketones, respectively. DCM was used as a solvent to mix with the internal standard, 1-hexanol, at a concentration of 1.04 g/L. The standard calibration curves were developed by calculating the quantification factor of the slope obtained from concentration versus GC area of above neat compounds with three replications. For biocrude oil and upgraded biocrude oil compositional analyses, a standard stock solution was prepared immediately before GC-MS operation by adding 10 μL of 1-hexanol into 800 μL of DCM. After vortexing, 35 μL of standard stock solution was mixed with 302 μL of biocrude oil or upgraded biocrude oil sample. A quantity of 1 μL mixed sample solution was injected into GC-MS after filtration with a 0.45 μm filter. The solvent delay was setup for 3 min to ignore DCM. The compounds were identified by matching fragmentation patterns with National Institute of Standards and Technology (NIST) mass spectral library. Each sample from HTL and HDO experiments was repeated thrice. The average result was reported with standard deviation.

**Table 1.** Summary of Product Yields under Various HTL and HDO Conditions

whole-stage HTL <sup>a</sup>				second-stage HTL <sup>b</sup>	whole-stage HTL-HDO <sup>c</sup>	second-stage HTL-HDO <sup>d</sup>
Product Yield (%)						
holding time (min)	15	30	60	30	240	240
catalyst		0.94 M K <sub>2</sub> CO <sub>3</sub>		N/A	5% Ru/C	5% Ru/C
gas	9.33 (0.67)	36.03 (1.33)	41.30 (1.33)	11.00 (1.17)	34.76 (1.79)	32.91 (2.25)
solid	8.03 (0.00)	6.67 (0.67)	5.33 (0.67)	15.89 (1.28)	4.01 (0.70)	7.42 (1.84)
biocrude oil	17.30 (0.67)	25.30 (1.33)	21.33 (0.67)	10.38 (1.48)	27.81 (2.46)	41.70 (0.67)
aqueous	65.34 (0.00)	32.00 (0.67)	32.04 (0.00)	62.80 (1.40)	33.42 (4.95)	17.97 (3.40)

<sup>a</sup>The yield of whole-stage HTL was calculated on the basis of dried raw sweet sorghum bagasse. <sup>b</sup>The yield of second-stage HTL was calculated on the basis of first-stage HTL solid product. <sup>c</sup>The yield of whole-stage HTL-HDO was calculated on the basis of solid and liquid products from whole-stage HTL. <sup>d</sup>The yield of second-stage HTL-HDO was calculated on the basis of solid and liquid products from second-stage HTL.



Table 2. Fuel Properties of Biocrude Oils Obtained from Different HTL Conditions<sup>a</sup>

catalyst	Whole-Stage HTL				Second-Stage HTL	Whole-Stage HTL-HDO	Second-Stage HTL-HDO	benchmark petroleum <sup>43</sup>
	0.94 M K <sub>2</sub> CO <sub>3</sub>		Nocatalyst		0.94 M K <sub>2</sub> CO <sub>3</sub>	5% Ru/C	5% Ru/C	
	holding time = 15 min	holding time = 30 min	holding time = 60 min	holding time = 30 min	holding time = 30 min	holding time = 240 min	holding time = 240 min	
C [%]	72.81 (0.25)	69.62 (0.34)	73.96 (0.41)	69.13 (0.29)	79.30 (0.53)	86.87 (2.12)	88.22 (2.28)	83–86
H [%]	7.46 (0.02)	7.24 (0.01)	7.66 (0.08)	6.86 (0.06)	8.37 (0.06)	9.06 (0.31)	9.11 (0.20)	11–14
N [%]	1.36 (0.06)	1.35 (0.02)	1.30 (0.02)	1.24 (0.02)	0.63 (0.03)	1.28 (0.02)	0.61 (0.03)	<1
O [%]	18.38 (0.24)	21.79 (0.33)	17.08 (0.49)	22.73 (0.33)	11.70 (0.54)	2.79 (1.91)	2.06 (1.82)	~0
O/C	0.19	0.23	0.17	0.25	0.11	0.03	0.02	~0
H/C	1.23	1.25	1.24	1.19	1.27	1.25	1.24	1.5–2.0
HHV [MJ/kg]	31.97	29.97	32.88	29.10	36.65	41.78	42.43	44

<sup>a</sup>Data shown in the parentheses are standard deviations with  $n = 3$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. Whole-Stage vs Second-Stage HTL Experiment.

**3.1.1. HTL Biocrude Oil Yield.** The biocrude oil yield increased up to 1.44 times in the presence of K<sub>2</sub>CO<sub>3</sub> catalyst, because of decreased aqueous product and solid yields (see Table 1). During HTL of lignocellulosic biomass, K<sub>2</sub>CO<sub>3</sub> catalyzed the hydrolysis of lignin and cellulose macromolecules into oligomers and monomers, thus promoting the following decomposition into a diversity of secondary small-molecular compounds through dehydration, dehydrogenation, deoxygenation, and decarboxylation reactions. Once produced on the basis of their activities, these small-molecular compounds experienced rearrangement reactions of condensation, cyclization, and polymerization and formed the majority of biocrude oil.<sup>40</sup> In addition, the solid product yield decreased by 58%, while the gas product yield increased by 2.27-fold, because of an alkali carbonate effect proposed by Appell.<sup>41</sup> This gasification effect was crucial for deoxygenation, but at the cost of carbon loss.<sup>13</sup> The yield trends of HTL with alkaline catalysts were similar to that of other studies conducted elsewhere.<sup>7,14</sup>

The effect of holding time on the biocrude oil yield of whole-stage HTL with alkaline catalyst was also studied. Biocrude oil yield increased by 46% from 15 min residence time to 30 min residence time and then decreased to 16% from 30 min residence time to 60 min residence time. The maximum biocrude oil yield of 25% was obtained at 30 min. A prolonged retention time suppressed the biocrude oil yield, as reported by Boocock<sup>19</sup> and Zhu.<sup>13</sup> The decline in biocrude oil yield with longer time could be due to the condensation and repolymerization reactions within the biocrude oil.<sup>23</sup> Although the detailed mechanism of biocrude oil decomposition are still unclear, our study confirmed an increase in gas yield with longer reaction time. The result further confirmed that the use of 0.94 M K<sub>2</sub>CO<sub>3</sub> had prevented the repolymerization reaction between hemicellulose decomposition intermediates and lignin unit derived from raw sweet sorghum bagasse. Therefore, the HTL condition of 350 °C, 30 min with 0.94 M K<sub>2</sub>CO<sub>3</sub> was the most suited conditions for maximum biocrude oil yield and thus was used as a basis for comparing the second-stage HTL to produce biocrude oil from lignin-rich sweet sorghum bagasse.

The lignin-rich sweet sorghum bagasse had 94% increase in lignin and 18% increase in cellulose content, compared with that of raw sweet sorghum bagasse. Table 1 summarized the HTL products yield for second-stage HTL of lignin-rich feedstock. The biocrude oil yield of second-stage HTL was increased by 49%, compared with that of whole-stage HTL.

The second-stage HTL biocrude oil yield of 38% was obtained from hemicellulose-free sweet sorghum bagasse and the yield was higher than reported elsewhere for pine wood,<sup>17</sup> birch wood,<sup>12</sup> sawdust,<sup>42</sup> and cornstalks.<sup>10</sup> The second-stage HTL process also reduced the aqueous product yield by 44%, compared with that of whole-stage HTL. In addition, it was found that there was no significant solid yield difference between the second-stage HTL and whole-stage HTL, which confirmed that the potential formation of char through cross-reaction and repolymerization between hemicellulose and lignin intermediates was suppressed from whole-stage HTL with the presence of K<sub>2</sub>CO<sub>3</sub>.<sup>17,18</sup>

**3.1.2. HTL Fuel Properties.** The elemental composition of biocrude oil from HTL experiments is summarized in Table 2. In the presence of 0.94 M K<sub>2</sub>CO<sub>3</sub>, ~43% of the carbon in the sweet sorghum bagasse was converted to biocrude oil after 30 min, which is 2.45 times more than that of noncatalytic biocrude oil yield. In the absence of K<sub>2</sub>CO<sub>3</sub>, a major fraction of the carbon was converted to carboxylic acid and ends up in the aqueous fraction of the biocrude oil.

The HHVs of biocrude oils ranged from 29.10 MJ/kg to 32.88 MJ/kg (Table 2), which almost doubled that of the sweet sorghum bagasse feedstock of 16.30 MJ/kg.

H/C and O/C ratios were two crucial factors in estimating the fuel combustion property. Fuels with higher H/C ratio and lower O/C were desirable for their higher energy density. In the presence of K<sub>2</sub>CO<sub>3</sub>, H/C ratios from 15 min to 60 min were maintained at the most consistent value of ~1.24. The O/C ratio increased at 15 min from 0.19 to 0.23 at 30 min and decreased 0.17 after 60 min. These O/C ratios decreased ~80% from sweet sorghum bagasse, because of the formation of highly oxygenated compounds during the HTL reaction, such as carboxylic acids in the aqueous phase and CO<sub>2</sub> in gas phase.

The elemental analysis of second-stage HTL biocrude oil is listed in Table 2. According to the Dulong Formula previously provided, the HHV of second-stage HTL biocrude oil was 36.65 MJ/kg, which is 22% more than that of whole-stage HTL biocrude oil. The O/C ratio of second-stage HTL biocrude oil was 0.11, which is 52% lower than that of whole-stage biocrude oil. The results further confirmed that the use of hemicellulose-free feedstock with reduced oxygen content in the second-stage HTL increased the biocrude oil energy density.

**3.1.3. HTL Biocrude Oil Composition.** The composition of biocrude oil from catalytic whole-stage HTL was quantitatively analyzed with GC-MS. More than two hundred compounds were identified. Cyclic ketones, phenols, and hydrocarbons

composed the majority, occupying more than 90% of total area from the chromatogram. These major compounds are listed in Table 3. The cyclic ketones accounted for 57%–75% of the

**Table 3. Major Compositions of Biocrude Oil from Whole-Stage HTL**

Catalytic ( $K_2CO_3$ ) Whole-Stage HTL Condition			
compound	Composition (mass %)		
	holding time = 15 min	holding time = 30 min	holding time = 60 min
<i>Cyclic ketones</i>	74.57	56.75	58.48
cyclopentanone, 2,5-dimethyl-	4.23	2.78	4.72
2-cyclopenten-1-one, 2,3-dimethyl-	5.11	2.51	1.64
2-cyclopenten-1-one, 2,3,4-trimethyl-	31.57	21.95	15.72
2-cyclopenten-1-one, 2,3,4,5-tetramethyl-	33.66	29.51	36.40
<i>Phenolics</i>	18.62	35.83	35.30
phenol	0.88	1.66	
phenol, 2-methyl-	0.00	2.43	0.99
phenol, 4-methyl-	3.21	5.21	3.06
phenol, 2,4-dimethyl-			13.59
phenol, 3,5-dimethyl-	8.54	10.65	
phenol, 2-ethyl-4-methyl-	1.84	1.46	2.16
phenol, 2-ethyl-5-methyl-		3.38	
phenol, 4-ethyl-3-methyl-			4.05
phenol, 2-methyl-5-(1-methylethyl)-	1.29	2.52	
thymol			3.67
other phenolics	2.86	8.51	7.78
<i>Hydrocarbons</i>	6.81	7.43	6.22
<i>Aromatic hydrocarbons</i>	4.61	7.43	5.07
1,3-dimethyl-1-cyclohexene	0.93		
toluene	0.65	1.21	0.55
1H-indene, 2,3-dimethyl-	2.22	1.32	2.24
1H-indene, 2,3-dihydro-1,6-dimethyl-		4.05	1.56
other aromatic hydrocarbons	0.81	0.85	0.71
<i>Alkanes</i>	2.20		1.15
pentadecane	1.20		0.72
heptadecane	1.00		0.43

total biocrude oil, mainly in the form of alkylated cyclopenten-1-one. This observation was consistent with Pedersen's report that methylated cyclopentenone was the most presented compound in distillation fraction of biocrude oil.<sup>44</sup> The abundance of these cyclic ketones with five carbon naphthenic ring backbones are potential precursors of aromatic hydrocarbons and also suggests a global route of ketonization from major intermediates.<sup>44</sup> As far as we have known, alkylated cyclopenten-1-ones were primarily generated from one of the cardinal intermediates, 5-hydroxymethyl furfural (5-HMF), which decomposed from the hydrolysis of cellulose and hemicellulose units, xylose and fructose,<sup>45</sup> and was further converted to cyclopenten-1-one through 1,4-benzenetriol.<sup>46</sup> Another formation pathway of alkylated cyclopenten-1-ones involved a series of ketonic decarboxylation, substitution, and condensation reactions from carbohydrates decomposed from carboxylic acids, such as lactic acid, formic acid, and acetic acid

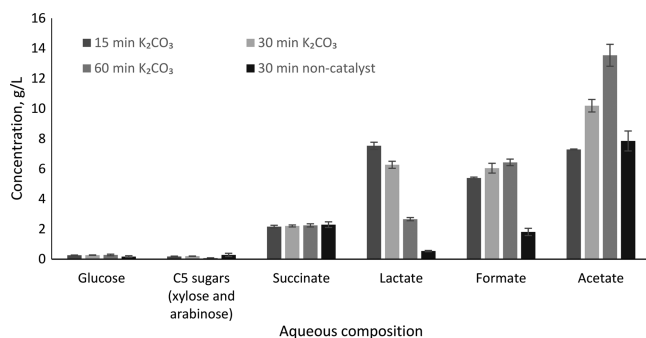
and propionic acid.<sup>47</sup> A minor source of cyclopenten-1-one was also reported from the decomposition of the lignin unit, catechol.<sup>48</sup> When the holding time was extended from 15 min to 30 min, the yield of methylated penten-1-one compounds decreased, followed by a slight enhancement after 60 min. Alkylated phenolics, which represent the second most prominent compound, formed from the decomposition of both structural carbohydrates and lignin through two discrete pathways. Concerning the mode of structural carbohydrates decomposition, similar to alkylated cyclopenten-1-one as described above, alkylated phenolics were another product from the rearrangement of 5-HMF and 1,4-benzenetriol.<sup>45</sup> Concerning the lignin decomposition mode, alkylated phenolics could be converted either through modification of a lignin unit or through an addition reaction of hydroxylated phenols, from the breakage of  $\beta$ -aryl and benzoyl ether bonds in lignin,<sup>35</sup> and C2–C6 oxides.<sup>49</sup> The maximum yield of hydrocarbons was 2%, obtained at 30 min with 0.94 M  $K_2CO_3$  as the catalyst. Negligible amounts of alkanes were identified under this condition. More than 68% of the identified hydrocarbons were in the form of aromatics. Fatty acids, such as *n*-hexadecanoic acid and 13-octadecenoic acid, that formed from residual wax in sweet sorghum bagasse were remarkably impacted by alkaline catalyst and were only observed in noncatalytic biocrude oil. It is proposed that the formation of fatty acids was suppressed at high pH levels in the presence of  $K_2CO_3$ . However, the mass percentages of fatty acids in noncatalytic biocrude oil was not determined, because of inconsistent standard curve of neat fatty acid compounds. The area percentages of whole-stage HTL biocrude oil composition is listed in the Supporting Information.

The biocrude oil composition from the second-stage HTL were analyzed and compared with that of whole-stage HTL (see Table 4). Ketone and phenol compounds constituted the majority of second-stage HTL biocrude oil by accounting for 44% and 47%, respectively. The cyclic ketones content was reduced by 49%, when compared with that of whole-stage HTL biocrude oil, as most ketone precursors were removed through the hydrolysis pretreatment of first-stage HTL. Methylated 2-Cyclopenten-1-one was still the most representative ketone compound. The content of phenolics increased by 30% from whole-stage HTL biocrude oil, which could benefit the downstream upgradation process. Alkylated phenolics represented 83% of all phenolics, and the major compounds of phenolics were quite similar to those of whole-stage HTL biocrude oil. The hydrocarbon content slightly increased; small fractions of benzenes were also detected. Generally, no substantial difference was observed on compositional distribution of biocrude oil after hemicellulose removal, which indicates that hemicellulose did not influence the biocrude composition. Therefore, our proposed approach of two-stage HTL improved the biocrude oil, with no negative effects on its quality.

**3.1.4. HTL Aqueous Composition.** The yields of major aqueous compounds are shown in Figure 3. Generally, the C5 and C6 monomer sugars from cellulose and hemicellulose decomposed to short chain carboxylic acids, typically, lactic acid, formic acid, and acetic acid. The accumulation of carboxylic acids gradually promoted the reaction atmosphere from weak alkaline ( $K_2CO_3$  added) or neutral (noncatalyst added) into weak acidic. This acidic condition inhibited the formation of lactate, which forms under alkaline or neutral conditions from pyruvaldehyde through glyceraldehyde and dihydroxyacetone decomposing from fructose.<sup>50</sup> The maximum

**Table 4. Comparison of Major Compounds in Biocrude Oils from Whole-Stage and Second-Stage HTL Experiments**

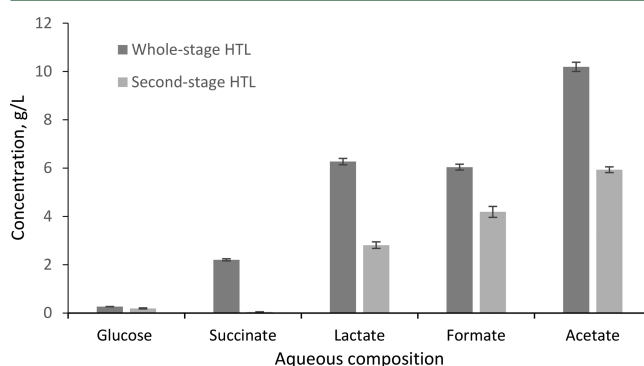
compound	Composition (mass %)	
	whole-stage HTL	second-stage HTL
<i>Straight ketones</i>		6.11
2-butanone		4.82
2-pentanone		1.29
<i>Cyclic ketones</i>	56.75	38.19
cyclopentanone, 2-methyl-		2.74
cyclopentanone, 2,5-dimethyl-	2.78	3.70
2-cyclopenten-1-one, 2,3-dimethyl-	2.51	4.33
2-cyclopenten-1-one, 2,3,4-trimethyl-	21.95	10.59
2-cyclopenten-1-one, 3,4,4-trimethyl-		7.20
2-cyclopenten-1-one, 2,3,4,5-tetramethyl-	29.51	9.64
<i>Phenolics</i>	35.83	46.53
phenol	1.66	3.03
phenol, 2-methyl-	2.43	2.97
phenol, 4-methyl-	5.21	5.00
phenol, 4-ethyl-	0.98	2.77
phenol, 2,4-dimethyl-	10.65	10.09
phenol, 2,4,6-trimethyl-		5.34
phenol, 2-ethyl-5-methyl-	3.38	2.61
phenol, 2-methyl-5-(1-methylethyl)-	2.52	
1,3-benzenediol, 4,5-dimethyl-	3.64	1.01
1,4-benzenediol, 2,3,5-trimethyl-	1.46	2.49
others phenolics	4.87	11.22
<i>Hydrocarbons</i>	7.43	8.20
toluene	1.21	
cyclohexene		1.15
1H-indene, 1,3-dimethyl-	1.32	0.86
1H-indene, 2,3-dimethyl-		1.96
1H-indene, 2,3-dihydro-1,6-dimethyl-	4.05	0.37
1H-indene,2,3-dihydro-2,2-dimethyl-		1.15
other hydrocarbons	0.85	2.71
benzenes		0.97

**Figure 3. Yields of major aqueous products after whole-stage HTL.**

yield of lactate was 7.53 g/L, obtained at 15 min in the presence of  $K_2CO_3$ . This yield decreased by 2.83-fold after 60 min. When  $K_2CO_3$  was not added, the lactate yield was reduced by a factor of 11.61, compared to that of catalytic HTL yield at 30 min. Acetate yield was found to increase with reaction time with a maximum yield of 13.54 g/L at 60 min. Acetate was mainly formed from cellulose to levoglucosan decomposition, which dehydrated from glucose.<sup>51,52</sup> The yield of acetate increased by 30% when  $K_2CO_3$  was added to noncatalytic whole-stage HTL, because of the formation of acetic acid influenced by the initial pH of the HTL reaction.<sup>51</sup> Formate was primarily formulated

through two pathways. One was through 5-HMF decomposing into formic acid and levulinic acid under acidic conditions; the other was from glucose decomposing to erythrose, which further decomposed to formic acid through glycolaldehyde under alkaline conditions.<sup>50</sup> In the presence of  $K_2CO_3$ , both pathways occurred with decreasing pH. Formate yield reached to 6.04 g/L at 30 min, which is 3.34 folds higher than that of noncatalytic condition. The yields of glucose, C5 sugars (xylose and arabinose), and succinate were relatively stable, with average yields of  $\sim 0.24$  g/L,  $\sim 0.16$  g/L, and  $\sim 2.20$  g/L, respectively. The low yields of sugars indicated that  $\sim 99\%$  of C5 and C6 sugars from hemicellulose and cellulose were decomposed. In addition, there were no furfural and 5-HMF detected from the above reaction conditions, because of their rapid decomposition to carboxylic acid, humus, and benzene-triols at 350 °C.<sup>50,53</sup>

Figure 4 shows a comparison of concentrations of major aqueous products between second-stage HTL and whole-stage

**Figure 4. Major compounds in aqueous phase from whole-stage HTL and second-stage HTL.**

HTL experiments. The yield of aqueous products from second-stage HTL decreased by 44%, compared to that of whole-stage HTL. The HPLC analysis of second-stage HTL aqueous compounds indicated that the decline mainly resulted from the reduction of carboxylic acids, primarily succinate, lactate, formate, and acetate, which decreased to 98%, 55%, 31%, and 42%, respectively. The removal of hemicellulose crucially suppressed the formation of carboxylic acids with a total difference of 11.72 g/L, which contributed to biocrude oil composition after second-stage HTL.

Therefore, one of the most important benefits of two-stage HTL process was the reduction of aqueous products, compared to that of whole-stage HTL. The majority of inexpensive carboxylic acids present in the whole-stage HTL aqueous product were extracted to sugar mixtures from the two-stage HTL approach with minimal carboxylic acids byproduct. The sugar mixtures derived primarily from hemicellulose could be further converted to value-added chemicals through downstream biorefinery and catalytic conversion pathways.

**3.2. Whole-Stage HTL-HDO versus Second-Stage HTL-HDO.** **3.2.1. HTL-HDO Upgraded Biocrude Oil yield.** The yields of products from whole-stage HTL-HDO and second-stage HTL-HDO are listed in Table 1. The biocrude oil yield from second-stage HTL-HDO was remarkably increased by 50%, and the aqueous product yield decreased by 46%, compared to that of whole-stage HTL-HDO. The gaseous product yields from both HDO processes were similar. It was also found that the solid product from second-stage HTL-HDO



increased to 7%, because of polymerization during the reduction process of ketones and phenols into hydrocarbons.

**3.2.2. HTL-HDO Fuel Properties.** The elemental compositions of upgraded biocrude oil (Table 3) indicated that the oxygen content was significantly reduced after HDO. The O/C and H/C ratios of both upgraded biocrude oils were comparable to that of petroleum crude oil.

There was not much difference in the HHVs of upgraded biocrude oils: 41.78 MJ/kg for whole-stage HTL-HDO and 42.43 MJ/kg for second-stage HTL-HDO. The HHVs of the upgraded oils were very similar to that of petroleum crude oil (44 MJ/kg, reported by Mortensen et al.<sup>43</sup>). The moisture contents of upgraded biocrude oil was 0.48% after whole-stage HTL-HDO and 0.41% after second-stage HTL-HDO, were reduced by 84% and 73% from whole-stage and second-stage HTL biocrude oils, respectively.

**3.2.3. HTL-HDO Upgraded Biocrude Oil Composition.** The major compositions of upgraded biocrude oils are presented in Table 5. After HDO, the target product of hydrocarbons separately accounted for 34% from whole-stage HTL-HDO upgraded biocrude oil and 96% from second-stage HTL-HDO upgraded biocrude oil. The hydrocarbon fractions were increased by 3.62- and 10.68-fold of their fractions in whole-stage and second-stage HTL biocrude oils, respectively. Our findings confirm that, after removing hemicellulose, the second-stage HTL biocrude oil from lignin-concentrated biomass was more favorable for hydrocarbon production. Based on the unit-weight of raw sweet sorghum bagasse, if all of the feedstock could be used for whole-stage HTL-HDO, the available lignin-rich solid fraction after first-stage HTL only accounted for 43% of the initial weight.<sup>32</sup> However, the yield of final product of hydrocarbon in upgraded biocrude oil approached 11% from sweet sorghum bagasse through second-stage HTL-HDO, which is ~78% higher than that obtained through whole-stage HTL-HDO. This remarkable improvement on hydrocarbon conversion further demonstrated the advantage of two-stage HTL-HDO. More importantly, the compositional complexity of hydrotreated products from two-stage HTL-HDO was significantly simplified and negligible straight ketones, alkylated cyclopentanones, and phenolics were observed. From a biofuel perspective, the chemically similar deoxygenated products provide a high-quality drop-in biofuel to a gasoline pool, because of high octane numbers.<sup>44</sup>

The conversion efficiency of hydrocarbon was the most significant difference between second-stage HTL-HDO and whole-stage HTL-HDO. Almost all ketones and majority of phenols in second-stage HTL biocrude oil improved the hydrocarbons yield after HDO. For alkylated cyclic ketones with sufficient reduction donor of H<sub>2</sub>, the compounds of methylated 2-cyclopenten-1-ones could either be deoxygenated to form cyclopentene or hydrogenated to form cyclopentanone and then reduced to form cyclopentane.<sup>54</sup> However, based on the GC-MS results, only 1,2,3-trimethyl-cyclopentene and ethylenecyclobutane were identified in the upgraded biocrude oil with mass yields of 0.39% and 2.15%, respectively. Therefore, it was inferred that the majority of methylated 2-cyclopenten-1-one compounds underwent an additional reaction route through reduction, cyclization with phenols, and a final conversion to form polycyclic aromatic hydrocarbons. This addition reaction route contributed to 49% of the aromatic hydrocarbons. As for the whole-stage HTL biocrude oil, it was found that 31% of the methylated 2-cyclopenten-1-one was hydrogenated to form cyclopentanone after HDO.

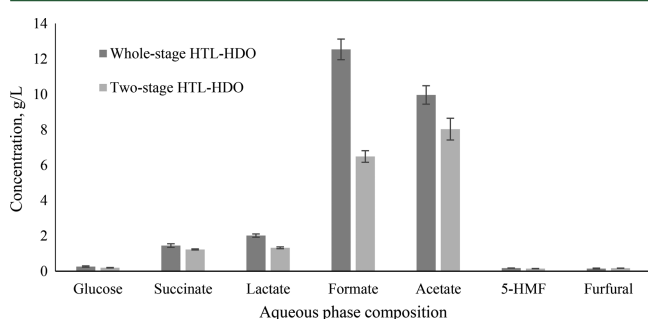
**Table 5. Comparison of Major Compounds in Upgraded Biocrude Oil from Whole-Stage HTL-HDO and Second-Stage HTL-HDO**

compound	Composition (mass %)	
	whole-stage HTL-HDO	second-stage HTL-HDO
<i>Ketones</i>	25.50	
2-butanone	10.22	
cyclopentanone, 2-methyl	8.09	
cyclopentanone, 1-ethyl-2-methyl	7.19	
<i>Phenolics</i>	40.17	4.25
phenol	3.52	
phenol, 2-methyl	4.81	
phenol, 3-methyl	7.57	0.51
phenol, 2,5-dimethyl	8.75	2.35
phenol, 2-ethyl-5-methyl	4.25	
phenol, 4-ethyl	7.73	
phenol, 2-propyl	3.54	
phenol, 2,3,5-trimethyl-		1.38
<i>Hydrocarbons</i>	34.33	95.75
<i>Aromatic hydrocarbons</i>	23.43	61.53
toluene	4.69	2.50
xylene	2.35	1.94
ethylbenzene	4.71	1.75
cyclohexene		2.97
benzene, 1-ethenyl-3-ethyl	4.17	7.38
benzene, 2-butenyl	3.74	0.60
indane	3.77	
benzene, 1-ethenyl-4-ethyl-		3.25
naphthalene		3.83
benzene, (2-methyl-1-butenyl)-		3.80
1H-indene, 2,3-dihydro-1,6-dimethyl-		7.31
1H-indene, 2,3-dihydro-2,2-dimethyl-		3.84
naphthalene, 2-methyl-		3.95
other aromatic hydrocarbons		23.93
<i>Alkanes</i>	10.90	34.22
pentadecane	2.93	2.30
heptadecane	3.41	1.39
eicosane		6.50
heptacosane		5.30
octadecane		2.40
tetracosane	2.63	2.02
9-octyl-heptadecane	1.93	
tridecane		1.84
other alkanes		6.95

There are two reaction pathways involved during the conversion of hydrocarbons from alkylated phenolics: one is to generate cyclohexenes through ring saturation, followed by dehydration reaction; the other favored the formation of aromatics through deoxygenation. More aromatics were identified than cyclohexenes. 1-Ethenyl-3-ethyl-benzene was the most represented aromatic hydrocarbon, accounting for 7.38%. The result has confirmed the proposed mechanism that, with the increased number of methyl substitutions on phenol backbones, it is more favorable for the formation of aromatics.<sup>55</sup> Massoth reported that methyl-substituted phenols showed resistance toward aromatics, because of electrostatic potentials,<sup>55</sup> and not all phenolics were completely converted to

hydrocarbons after the HDO process. Long-chain alkanes were another important composition of hydrocarbons, accounting for one-third of them. Approximately 11% of whole-stage HTL-HDO upgraded biocrude oil and 29% of second-stage HTL-HDO upgraded biocrude oil were composed of long-chain alkanes, ranging from C12 to C27. Rather than forming from fatty acids decarboxylation, which was undetectable from catalytic biocrude oil, it is proposed that those long-chain alkanes formed from ring scission of aromatic hydrocarbons.

**3.2.4. HTL-HDO Aqueous Product Composition.** Major compounds in HDO aqueous products are shown in Figure 5.



**Figure 5.** Major compounds in aqueous phase from whole-stage HTL-HDO and second-stage HTL-HDO.

Sugars and their primary intermediates (5-HMF and furfural) were detected in small amounts, ranging from 0.14 g/L to 0.26 g/L. Carboxylic acids were still the prominent compounds. The yields of succinate, lactate, formate, and acetate from second-stage HTL-HDO were 1.23 g/L, 1.32 g/L, 6.48 g/L, and 8.03 g/L, respectively, and they were reduced between 15% and 48%, compared to that of whole-stage HTL-HDO. This yield reduction was not only due to less carboxylic acid being produced from second-stage HTL, but also less alkylated cyclopenten compound formation from lignin-rich biomass and they were further reduced into aromatic hydrocarbons and carboxylic acids through decarbonylation during HDO.<sup>50</sup> It was also found that, after the HDO process, the concentrations of formate increased 1.08-fold and 0.55-fold from the whole-stage and second-stage HTL aqueous phase, respectively. However, acetate concentrations did not show remarkable increases. It is theorized that radical carboxyl from deoxygenation crack was more likely to form formate rather than polymeric carbon carboxylic acids, although research is required to confirm this reaction pathway.

#### 4. CONCLUSIONS

A two-stage HTL-HDO process was successfully developed and demonstrated in this study. The quality and the compositions of upgraded biocrude oil with 96% hydrocarbon content from second-stage HTL-HDO were substantially improved, compared with that from whole-stage HTL-HDO. It was further illustrated that the two-stage HTL process substantially increased the hydrocarbon precursors, such as alkylated phenolics compounds in the biocrude oil. Simultaneously, the yields of oxygenated compounds with carboxyl and carbonyl groups remarkably declined, because of the absence of hemicellulose intermediates. The second-stage HTL biocrude oil was more suited for HDO and can be further upgraded and distilled to produce drop-in biofuels. From the given amount of sweet sorghum bagasse, ~11% hydrocarbons were yielded through the second-stage HTL-HDO process, which is 78%

higher than that of whole-stage HTL-HDO. This result illustrated the advantage of employing two-stage HTL-HDO processes for hydrocarbon production, as well as the additional co-product of sugars mixture from lignocellulosic biomass feedstock; moreover, these could contribute to the large-scale production of multiple catalytic thermal products including drop-in biofuels and value-added sugar-based chemicals.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.8b00669.

Information regarding gas product analysis from HTL and HTL-HDO processes; gas product components of HTL and HDO reactions (Table S1); and biocrude oil composition of whole-stage HTL (Table S2) (PDF)

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##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

The project was financially supported, in part, by USDA-NIFA Sustainable Bioenergy Research (Grant No. GEOX-2010-03868) via Fort Valley State University.

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