Full Length Article

Biocrude from pretreated sorghum bagasse through catalytic hydrothermal liquefaction

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HIGHLIGHTS

- Among six catalysts, K_2CO_3 was the best leading to the highest biocrude yield of 61.8%.
- Biocrude from K_2CO_3 had a HHV of 33.1 MJ/kg and low content of N and S.
- Phenolics were the most abundant compounds identified in the three biocrudes with the highest yields.
- The aqueous phase samples analyzed had COD of 20,000–26,000 mg/L and 5–65 mg/L of TN and TP.

ARTICLE INFO

ABSTRACT

For the purpose of producing biocrude from pretreated and washed sweet sorghum bagasse, hydrothermal liquefaction (HTL) was conducted with six different catalysts at two temperatures. The six catalysts were: K_2CO_3, KOH, formic acid, Ni/Si—Al, Ni_2P and zeolite. The two temperatures were 300 and 350 °C. Based on two selection criteria, high yield of biocrude and low yield of biochar, K_2CO_3, KOH, and Ni/Si—Al were identified as the best catalysts which led to biocrude yields of 61.8%, 42.3% and 45.0% at 300 °C, respectively. As the best catalyst, K_2CO_3 led to biocrude samples with higher heating values (HHVs) of 33.1 MJ/kg. This biocrude had high carbon content and low contents of nitrogen and sulfur based on elemental analysis. However, the relatively high content of oxygen around 15% requires the biocrudes to be upgraded before refinery ready. Key compounds identified in these biocrudes will assist future effort in upgrading. Overall, this study proved that the pretreated bagasse is a suitable feedstock for HTL for generating biocrude. Through a simple dilute acid pretreatment step and HTL of the resulting solid, every component of sorghum bagasse can be used for producing biofuels.

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1. Introduction

To maintain energy sustainability, increase use of renewable transportation fuels and reduce emissions from combusting fossil fuels at a global level, liquid biofuels, such as ethanol, diesel, gasoline and jet fuel from renewable and sustainable resources must be produced at a price that is competitive to petroleum derived fuels. Based on this motivation and market need, a straightforward but highly efficient process to produce biodiesel from an oleaginous yeast strain, *Cryptococcus curvatus* grown on hydrolysate of sweet sorghum bagasse was developed. The three steps: pretreatment through using 0.5% sulfuric acid at 121 °C for 1 h, extensive wash to recover fermentable sugars and enzymatic hydrolysis of the remaining bagasse residue released 50.2%, 36.3%, and 5.7% of theoretically available sugars in sorghum bagasse, respectively [1]. The yeast strain thrived on the hydrolysates and accumulated lipids to a content of 48%. Through a one-step *in-situ* transesterification reaction using microwave energy, 92.0% of lipids in wet cells of *C. curvatus* were converted to crude biodiesel [2].

Technically, the bagasse-to-biodiesel pathway is certainly ready to be tested at a scaled-up level. Economically, however, the pretreated and washed bagasse generated from this pathway needs to handled properly. It needs to be noted that this bagasse was not hydrolyzed by cellulase enzymes considering high cost associated with this step and the low yield of sugars. To utilize this

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material, we seek to employ hydrothermal liquefaction (HTL) to convert bagasse biomass to biocrude. On one hand, compared with other thermochemical processes, HTL is conducted at a relative low temperature of 250–374 °C under a pressure of 4–22 MPa [3–8]. Furthermore, this process is favorable for feedstocks with high moisture content since it removes the need for pre-drying [5,7,9]. Thus, HTL is an excellent choice for converting the pretreated and washed bagasse with a moisture content of around 80%.

For the purpose of producing biocrude, HTL has been investigated to liquefy several biomass materials, such as swine manure [10], wood flour [11], sugar beet pulp [12], garbage [13], and microalgae [14]. The biocrude produced via HTL generally has a higher heating value (HHV) of 30–36 MJ/kg and a lower oxygen content of 10–20% from the biomass feedstocks normally possessing a HHV of 10–20 MJ/kg and an oxygen content of 30–50% [15]. The reported oil yield, however, varies broadly from 12% to 75% depending on the feedstock tested and HTL operating conditions.

Yield of biocrude from HTL can be affected by several factors. As a thermal process, temperature has been recognized as the most important one impacting the final oil production [16,17,3,18]. At temperatures lower than 280 °C, incomplete decomposition of individual biomass components suppresses the bio-oil yield [3]. At too high a temperature, above 350 °C, however, oil yield is also lowered. This is due to: first, the secondary decomposition [9,19,20] and series of gasification reactions become active at high temperatures, which lead to the formation of gases [18,21]; second, at high temperatures, recombination of free radicals leads to formation of char [5,22]. Thus, temperature for HTL of biomass materials has been recommended in the range of 300–350 °C. In several studies by different researchers [23–26], temperature range of 300–315 °C was found to be suitable for efficient production of liquid oils from lignocellulose biomass. A high yield of acetone soluble biocrude at approximately 76% at 300–310 °C was reported in [25].

Besides temperature, catalysts have been proven to play significant roles in increasing oil yield and improving oil quality. Various catalysts, such as organic acid (formic acid, acetic acid), alkaline (potassium hydroxide), sodium carbonate, and metals have been tested for different biomass feedstocks. The exact effect varies significantly among different catalyst types and characteristics. In the case of catalytic HTL of *Chlorella vulgaris* and *Spirulina* sp. the addition of organic acids has a beneficial effect on oil yield and boiling point distribution of the biocrude products [27]. Another study claimed that a maximum bio-oil yield of 25.8% is obtained at a reaction temperature of 360 °C and a holding time of 50 min using 5% Na_2CO_3 as a catalyst using *Dunaliella tertiolecta* residue left after lipid extraction [28]. Regarding *Dunaliella salina*, addition of a solid catalyst of Ni/REHY results in a significant increase of the biocrude yield [29]. Thus, for specific biomaterials, the optimum catalyst needs to be identified through experimental tests.

In addition to temperature and catalysts, biomass particle size may also impact oil yield since small particles having larger surface areas may have better accessibility to water for achieving higher degree of hydrolysis and fragmentation. However, as sub/supercritical water overcomes the heat transfer limitation in hydrothermal liquefaction, particle size is suggested to be a minor factor [25]. A particle size between 4 and 10 mm is suitable for use in liquefaction to overcome heat and mass transfer constraints [3]. This size requirement eliminates the need for costly grinding. Additionally, from most reported studies, pressure and the presence of a reducing gas (hydrogen and/or carbon monoxide) are all secondary parameters. Their effects are either minor or negligible for oil yield [5,6,30,31].

At the time of writing, no studies have liquefied sorghum bagasse, not to mention the bagasse remaining after dilute acid pretreatment and washing. Thus, for this study, we aimed to screen a total of six catalysts at two temperatures for achieving the highest yield of biocrude from the pretreated and washed bagasse. Based on biocrude yields, the top three oil samples were characterized by GC/MS and analyzed for elemental compositions. The corresponding aqueous phase samples were characterized too in terms of chemical oxygen demand, total nitrogen, total phosphorous, ammonia nitrogen and metals as detailed in the following.

2. Material and methods

2.1. Source of sorghum bagasse and pretreatment

Sweet sorghum bagasse was collected from the Hubert Farms in Ferdinand (IN, USA) after juice was squeezed out of the stalks. Once bagasse arrived in our laboratory, it was dried at room temperature for one week. Dried bagasse was cut and ground by a cutting mill (Thomas Wiley Model 4, Arthur H. Tjomas Co., Phil, PA, USA). A domestic coffee grinder (Fresh-Grind Coffee Grinder, Hamilton Beach Brands, Inc., Southern Pines, NC, USA) was then used to grind the milled bagasse to sizes less than 40 mesh (<420 μm). The resulting bagasse having a moisture content of approximately 11% was stored in Ziploc bags at room temperature.

To pretreat the bagasse for the purpose of releasing fermentable sugars, a procedure reported previously was adopted [1]. Briefly, to 10 g of dry bagasse samples in a 250-mL Erlenmeyer flask, 100 mL of sulfuric acid (0.5% (v/v)) was added. The mixture was then autoclaved at 121 °C for 1 h. After pretreatment, the cooled samples were centrifuged at 4000 rcf for 10 min. The solid portion was washed by distilled and deionized water (DDW) thoroughly, dried in a fume hood at room temperature for two days and then analyzed in terms of moisture content and composition according to a protocol explained in the following. The untreated or raw bagasse was analyzed in the same way.

2.2. Hydrothermal liquefaction (HTL) of pretreated bagasse

For the purpose of achieving the highest yield of biocrude, we aimed to evaluate the effects from six catalysts. These six included: (1) three homogeneous catalysts: formic acid, potassium carbonate (K_2CO_3), and potassium hydroxide (KOH), each at 1 mol/L concentration and (2) three heterogeneous catalysts, nickel phosphide (Ni_2P); nickel on silica alumina (Ni/Si—Al) and zeolite (ZSM-5, Yellow crystalline powder, 400–570 M ratio SiO_2/Al_2O_3), each at 2% dry wt%. All catalysts having the highest purity were purchased from either Sigma-Aldrich (St. Louis, MO, USA) or Fisher (Thermo Fisher Scientific, Rochester, NY, USA). For each catalyst and the controls without a catalyst, two temperatures of 300 and 350 °C were tested with a bagasse content of 20% (dry wt%) in a 25-mL tubular reactor made from stainless steel. The reactor was heated up to target temperatures at a ramping rate of 25 °C/min with a fixed retention time of 1 h. A total of 28 runs were performed considering that each tested condition was studied at two replicates.

Upon completion of a HTL run and after the reactor was cooled to room temperature, a total volume of 75 mL of dichloromethane (DCM) (Thermo Fisher Scientific, Rochester, NY, USA) was added to the reactor in three times to recover all content to an Erlenmeyer flask. The mixture in the sealed flask was left in the fume hood at room temperature for 4 h to ensure maximum biocrude dissolution in DCM. The whole content was then filtered through quantitative filter paper, Grade 42 (2.5 μm, Whatman, Maidstone, United Kingdom). The solid fraction remained on the filter paper was dried at 105 °C overnight, weighed and was referred to as biochar. The liquid fraction was separated further in a separatory funnel. The bottom layer was referred to as DCM soluble and the top layer as water soluble. The DCM soluble phase was transferred to a Rotovap