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Hydrothermal liquefaction of sewage sludge under isothermal and fast conditions

Lili Qian [a,b], Shuzhong Wang [b], Phillip E. Savage [a,*]

[a] Chemical Engineering Department, Pennsylvania State University, University Park, PA 16802, USA
[b] Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

HIGHLIGHTS

- First application of fast HTL and different organic solvents for sewage sludge.
- Showed that water loading in reactor can influence product yields.
- Highest biocrude yield and energy recovery achieved with dichloromethane.
- Fast HTL produces biocrude with higher H/C and O/C ratios and lower N/C ratio.
- Additives (K_2CO_3, Na_2CO_3, MoO_3-CoO/γ-Al_2O_3 and Ru/C) decrease the biocrude yield.

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ABSTRACT

We investigated the effects of water loading, sludge moisture content, recovery solvent, and additives on the product yields and compositions from isothermal (673 K, 60 min) and fast (773 K, 1 min) hydrothermal liquefaction (HTL) of sewage sludge. The water loading (which affects pressure within the reactor) plays a small role in product yields. The sludge moisture content had a larger effect with the highest biocrude yields (26.8 wt% from isothermal HTL and 27.5 wt% from fast HTL) being produced from sludge that was 85 wt% moisture. The HTL biocrude from sludge mainly contains long-chain aliphatic hydrocarbon moieties and aliphatic acids. Dichloromethane recovered more biocrude and energy content (~50%) than did the other solvents tested. Added K_2CO_3, Na_2CO_3, HCOOH, CH_3COOH, MoO_3-CoO/γ-Al_2O_3 and Ru/C significantly decrease the biocrude yield when their loadings are 50 wt% of the dried sludge. The additives, excepting carbonates, enhance gasification of sludge.

1. Introduction

Sewage sludge is a by-product of wastewater treatment. It contains proteins, lipids, fiber, non-fibrous carbohydrates, and ash (Suzuki et al., 1988). Land application, land filling, and incineration are the major sewage sludge treatment methods in the US (Gude, 2015). All of these methods require energy inputs for drying and also produce secondary pollution. Hydrothermal liquefaction (HTL) is a thermochemical process that directly converts wet biomass to energy-dense fuel precursors. Sewage sludge is readily available in large volumes and unlike bioenergy feedstocks such as microalgae, does not require cultivation. Thus, it might be a promising feedstock for HTL.

Previous work showed that sludge is amenable to HTL treatment. Biocrude yields ranging from 10 to 45 wt% have been reported for HTL temperatures ranging from 523–673 K (Inoue et al., 1997; Malins et al., 2015; Suzuki et al., 1990, 1988; Vardon et al., 2011; Wang et al., 2013; Yokoyama et al., 1987; Zhai et al., 2014). All of these previous studies used long holding times (30–60 min) and, at times, slow heating rate. Recently, however, fast HTL (Faeth et al., 2013) has emerged as a means of converting wet biomass to biocrude via rapid heating in tens of seconds rather than isothermal treatment for tens of minutes.

To the best of our knowledge, there is no prior work on fast HTL of sludge. The work herein fills that gap by comparing conventional isothermal HTL (673 K and 60 min) with fast, non-isothermal HTL (set-point temperature at 773 K and 1 min). The effect of water loading in the reactor and sludge moisture content were investigated under both conditions. Furthermore, we compared the effect of various solvents on the recovered biocrude yield and composition. Previous studies used exclusively dichloromethane. Finally, we examine influences of alkalis (K_2CO_3 and Na_2CO_3), organic acids

* Corresponding author.
E-mail address: psavage@psu.edu (P.E. Savage).

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(HCOOH and CH_3COOH), and transition metals or metal oxides (MoO_3-CoO/Al_2O_3 and Ru/C) on product distributions.

2. Materials and methods

2.1. Materials

Sewage sludge was obtained from a wastewater treatment plant in State College, PA, USA. The sludge is the original by-product of wastewater treatment. The moisture content of the sludge was determined to be 97.8 wt% by drying it at 343 K for 96 h. The sludge was 46.5 wt% C, 6.99 wt% H, 2.14 wt% N, 0.85 wt % S, and 10.3 wt% ash. The oxygen content, by difference, was 33.3 wt% and the organic content was 89.7 wt%. The higher heating value, as estimated by the Dulong formula, was 19.9 MJ kg^{-1}.

HPLC grade dichloromethane (DCM), methyl *tert*-butyl ether (MTBE), methyl isobutyl ketone (MIBK), hexane, xylenes, chloroform, methanol, ethanol, and acetone purchased from EMD Millipore Co. were used for recovery of biocrude. Analytical grade K_2CO_3, Na_2CO_3, HCOOH and CH_3COOH purchased from EMD Millipore Co. severed as acid and alkali additives. MoO_3-CoO/Al_2O_3 (cobalt oxide 3.4–4.5%, molybdenum oxide 11.5–14.5%, on alumina, purchased from Alfa Aesar) and Ru/C (5% wt% loading ruthenium on carbon, purchased from Aldrich) were employed as metal oxide and metal additives.

2.2. Experimental setup and procedures

4.1 mL mini batch reactors assembled from a 316 SS 1/2 in. Swagelok® port connector and two caps were used for HTL experiments. Reactors were loaded with carefully weighed amounts of dried sludge and deionized water, as well as additives when desired. Water and sludge loadings were determined so as to give the desired vol% water and solids loading (wt%) in the reactor. The vol% water is the percentage of the initial reactor volume that is occupied by water at the room-temperature loading conditions. This variable influences the reactor heat up (more water heats more quickly) and the pressure within the reactor at a given temperature. Additive loading was fixed at 10 or 50 wt% of the dried sewage sludge. The Supplementary material shows the loading details for the experiments.

After being loaded, the reactors were sealed, agitated by hand, and sonicated in a 1.9 L Fisher Scientific ultrasonic bath (Model: CPX1800) for better mixing. A proxy reactor was used to measure the reactor temperatures during heat up. The proxy reactor was fashioned and loaded with water just as the aforementioned reactor but it also included an Omega Engineering, Inc. 1/8 in. K-type thermocouple. The thermocouple tip was placed 2 mm above the bottom of the reactor interior to ensure it would always be immersed in water. An Omega Engineering, Inc. UWBT-TC-UST-NA data logger recorded the temperature inside the proxy reactor every 0.1 s. Detailed temperature profiles can be found in the Supplementary material.

The schematic diagram of this mini batch reaction system is shown in Fig. 1. In this system, a preheated Techne IFB-51 sand bath was used to heat the reactor. When the sand bath equilibrated at the set-point temperature, reactors were inserted into the sand. We choose two conditions: isothermal HTL (sand bath set-point temperature of 673 K and a holding time of 60 min) and non-isothermal, fast HTL (sand bath set-point temperature of 773 K and a holding time of 1 min). The critical temperature, pressure and density of water are: 674.1 K, 22.1 MPa, 322 kg m^{-3}, respectively (NIST, 2013).

After the desired holding time, the reactors were placed in a bucket filled with ice and tap water. After 10 min, the external

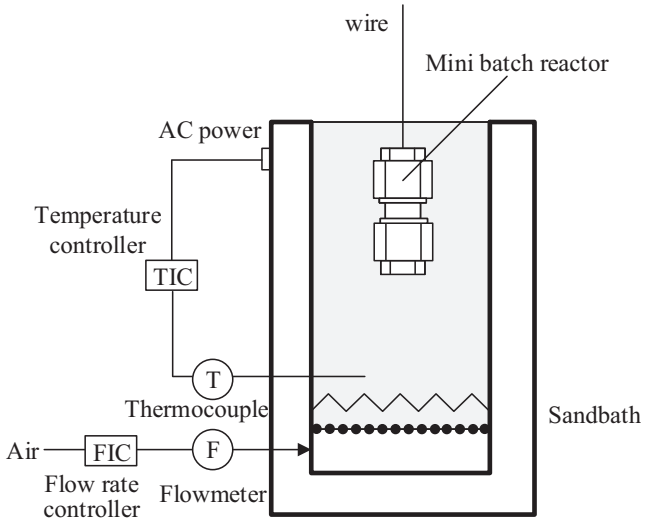

Fig. 1. Schematic diagram of the mini batch reaction system.

reactor walls were rinsed with tap water and dried by air and paper towels to remove residual sand particles and water. After 3 h, each reactor was tapped five times with a hammer to expel CO_2 dissolved in the aqueous phase and dislodge biocrude sticking in the caps. The reactors were opened with a torque wrench. We recorded the difference in the mass of the reactor pre- and post-opening and took this difference as the mass of gas formed.

The Supplementary material shows detailed procedures for product separation and extraction. When DCM, MTBE, MIBK, hexane, xylenes and chloroform were applied as solvents for recovering the biocrude, the reactor contents were first poured into a pre-weighed conical tube and then the reactor was washed with approximately 12 mL of the solvent in small aliquots to recover the biocrude. These washings were transferred to the same test tube as the reactor contents. The conical tube was mixed with a vortex mixer at 3000 rpm for 10 s and centrifuged at 1500 rcf for 3 min. To recover the aqueous and organic phases, the aqueous phase was transferred via pipet to a pre-weighed glass tube. Filtration was applied to separate solids from the organic phase. These solids would contain additives in some experiments. After filtration, the pre-weighed filter paper was washed with the desired solvent in small aliquots until the rinsings were clear. The conical tube, which contains some solids adhering to the wall, was dried together with the filter paper at 343 K for 48 h to determine the solids mass.

When methanol, ethanol and acetone were used as solvents, they did not come in contact with the aqueous phase because these solvents are miscible with water. Instead, we first poured the aqueous phase from the reactor to a pre-weighed conical tube and centrifuged it at 1500 rcf for 3 min to separate solids. Otherwise, the procedure is the same as previously described. In this case, solids separated from the aqueous phase and organic phase and remaining on the filter paper were dried at 343 K for 48 h to determine the solids mass.

The tube containing the aqueous phase was dried in an oven at 343 K for 72 h and then weighed. Biocrude was recovered by evaporating the organic solvents with 99.998% pure N_2 at 0.23 MPa using a Labconco evaporator (Model: 73200). Table 1 shows the temperatures and times used for evaporating the different solvents. We verified that these conditions provided complete removal of the various solvents by weighing the samples during the drying process until the tube masses changed by less than 0.5 mg.