Fuel 200 (2017) 146–152

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Efficient renewable fuel production from sewage sludge using a supercritical fluid route

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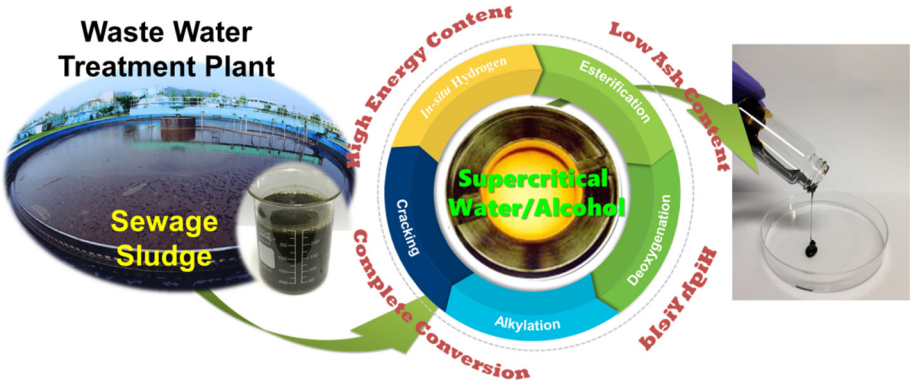
HIGHLIGHTS

- Non-catalytic, non H_2 sewage sludge liquefaction was held in supercritical fluids.
- High bio-oil yields of 87.8 wt% and HHV of 34.6 MJ kg^{-1} were achieved.
- The presence of water increases the conversion up to 96% and HHV up to 37.3 MJ kg^{-1}.
- Ester and nitrogenated compounds were the major compounds in the bio-oil.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 November 2016
Received in revised form 17 March 2017
Accepted 19 March 2017
Available online 27 March 2017

Keywords:
Sewage sludge
Liquefaction
Bio-oil
Supercritical fluid
Non-dry sludge

ABSTRACT

Conversion of sewage sludge into fuel was investigated using a catalyst- and external hydrogen-free supercritical fluid route. When dried sewage sludge was treated in supercritical ethanol, an extremely high bio-oil yield of 87.8 wt% and a remarkable higher heating value (HHV) of 34.6 MJ kg^{-1} were obtained. The possibility of using non-dried sewage sludge as a fuel source was tested using various alcohol–water mixtures; the presence of water resulted in an almost complete (96%) conversion and high HHVs of 36.8 and 37.3 MJ kg^{-1} for methanol–water (3:7, v/v) and ethanol–water (3:7, v/v) mixtures, respectively. The main chemical compounds in the bio-oils were found to be esters and nitrogenated species. Plausible reaction mechanisms for sewage sludge conversion in each supercritical fluid are discussed.

1. Introduction

Owing to its significant organic matter content (e.g., carbohydrates, proteins, lipids, and nucleic acids), with an energy content comparable to that of typical biomass (12–20 MJ kg^{-1}) [1], sewage sludge represents a very promising candidate for the production of alternative fuels for electricity and transportation [2]. Various thermochemical approaches have been investigated for utilizing the organic matter contained in sewage sludge [3–5]. Even though an appreciable amount of bio-oil can be obtained by pyrolysis (50–80 wt% on a dry ash-free basis) [6], the approach requires an energy-intensive drying pretreatment of wet sewage sludge with a water content of up to 80 wt%. The considerable energy consumption of such drying processes makes pyrolysis less attractive for practical scale applications.

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http://dx.doi.org/10.1016/j.fuel.2017.03.061
0016-2361/

On the other hand, liquefaction, in which a suitable solvent is used for extracting and/or decomposing the organic matter present in sewage sludge, has several advantages over pyrolysis, as a drying pretreatment is not necessary and lower temperatures can thus be used. So far, several studies have investigated the liquefaction of sewage sludge in sub- or supercritical water (subH_2O or scH_2O, respectively) [7]. The calorific value of bio-oil shows a moderate increase upon raising the temperature of the gasification regime to 500 °C using external molecular hydrogen or a catalyst (e.g., K_2CO_3, $Ca(OH)_2$, $Ba(OH)_2$, Na_2CO_3, NaOH, $FeSO_4$, FeS, Raney Ni, $FeSO_4$, MoS_2, and sewage sludge-based activated carbon) [2,7–11]. For example, a high calorific value of 39.1 MJ kg^{-1} was obtained in the presence of an activated carbon catalyst based on sewage sludge [10]. Use of organic solvents such as methanol [12], ethanol [5,11–13], acetone [12], tetralin [14], and 2-methyltetrahydrofuran (MeTHF) [14] instead of water has been shown to improve the yield and properties of bio-oil to some degree. Even though previous studies have demonstrated the significant potential of sewage sludge liquefaction for the production of liquid fuels, the use of external molecular hydrogen, heterogeneous catalysts, and expensive chemicals (e.g., tetralin and MeTHF) increases the processing costs, which prevents the practical scale implementation of liquefaction for the production of bio-oil. In order to improve the energy efficiency of the sewage sludge conversion process, methods based on the wet sewage sludge discharged from wastewater treatment plants could represent a valid feed. Despite the potential value of non-dried sewage sludge as a feed in supercritical alcohol-based conversion processes, the only published study on these systems [11] was negatively affected by the use of expensive ethanol and reported a low bio-oil yield (38 wt%).

In this study, we investigate the feasibility of utilizing the liquefaction of wet sewage sludge in supercritical methanol and ethanol (scMeOH and scEtOH, respectively) for the high-yield production of bio-oil with high calorific values and low acidity. In order to study the fundamental liquefaction behavior of sewage sludge in different solvents (water, methanol, and ethanol), dried sewage sludge was liquefied under various operating conditions (involving different temperatures, residence times, and concentrations). Then, the feasibility of using non-dried sewage sludge as a fuel source was tested using a methanol–water or ethanol–water mixture as the liquefaction solvent. Previously, we demonstrated that scEtOH in the absence of water could depolymerize highly recalcitrant lignin into high-yields of bio-oil [15]. The favorable physical properties of supercritical fluids (high diffusivity and density, low viscosity, and rapid rates of mass and heat transfer), as well as the unique reactivity of supercritical alcohols (e.g., *in situ* hydrogen donation [16,17], alkylation [18,19], hydroxyalkylation [20,21], deoxygenation [22,23], and esterification [24]), resulted in a high bio-oil yield of 87.8 wt% with a high calorific value of 34.6 MJ kg^{-1} from the liquefaction of dried sewage sludge in scEtOH under optimized conditions. On the other hand, a moderate bio-oil yield of 51.0 wt% with a comparable calorific value of 34.1 MJ kg^{-1} was obtained in supercritical methanol (scMeOH). When a 3:7 (v/v) methanol–water mixture with low methanol content was used, a moderate yield of bio-oil (52.5 wt%) with a high calorific value (36.8 MJ kg^{-1}) could be achieved without using external hydrogen and catalysts. These values are comparable to those previously reported for catalytic liquefaction using dried sewage sludge and organic solvents (entries 4, 5, 7, 9, and 11 in Table S1, Supporting Information) [5,11–14]. Unlike these previous studies, the present work focuses on alcohol–water mixtures as liquefaction solvents: we assess the feasibility of using an economically viable solvent and removing the expensive drying pretreatment in order to achieve the high-yield production of bio-oils with excellent properties.

2. Experimental

2.1. Materials

Sewage sludge slurry was collected from a wastewater treatment plant located in Suwon, South Korea. The slurry was initially dried at 105 °C for 12 h, followed by tests performed to assess the reactivity of three supercritical fluids (water, methanol, and ethanol) and the effect of water content associated with the use of alcohol–water mixtures. Table S2 lists the properties of the dried sewage sludge. The combustion behavior of the dried sewage sludge is illustrated in Fig. S1. HPLC-grade methanol, ethanol, and acetone were purchased from Honeywell Burdick and Jackson® (USA). Deionized water (HPLC grade) was purchased from Wako Pure Chemical Industries, Ltd. (Japan). High-purity nitrogen (99.99%), used for purging the reactor, was purchased from JC Gas Company (South Korea).

2.2. Liquefaction procedure

Liquefaction experiments were conducted in a stirred SUS 316 reactor with an inner volume of 140 mL. The reactor was equipped with a magnetically driven stirrer (HM-3200, Hanwoul Engineering Inc., South Korea). The temperature of the reactor was controlled using a heat furnace and cartridge heaters inserted in the reactor wall. The solvent filling ratio in the reactor was fixed to 50 vol%. After loading the sewage sludge and solvent, the reactor was sealed and flushed three times with N_2 to remove residual air, followed by pressurization with N_2 at 1 MPa. The mixture was stirred at 500 rpm inside the reactor and heated to the target temperature at an average heating rate of 15 °C min^{-1}. The time required for heating and cooling was not included in the reaction time. Fig. S2 shows the protocol employed for the separation of gas, liquid, and solid products after liquefaction. A detailed description of the separation protocol is given in the Supporting Information.

2.3. Product analysis and characterization

The yields of bio-oil, gas products, and solid residue were calculated using Eqs. (1)–(3), respectively. The labels "dafb" and "db" used in the equations stand for "dry ash-free basis" and "dry basis", respectively.

$$\text{Bio}-\text{oil yield}(\text{wt}\%) = \frac{\text{Weight of bio}-\text{oil(dafb)}}{\text{Weight of sewage sludge(dafb)}} \times 100 \quad (1)$$

$$\text{Gas yield }(\text{wt}\%) = \frac{\text{Weight of produced gas}}{\text{Weight of sewage sludge(dafb)}} \times 100 \quad (2)$$

$$\text{Solid residue yield}(\text{wt}\%) = \frac{\text{Weight of solid residue}}{\text{Weight of sewage sludge(db)}} \times 100 \quad (3)$$

$$\text{Conversion}(\%) = \frac{\text{Weight of sewage sludge(dafb)} - \text{weight of coke}}{\text{Weight of sewage sludge(dafb)}} \times 100 \quad (4)$$

The yield of coke formed during liquefaction was determined by combustion of the organic species remaining in the solid residue using thermogravimetric analysis (TGA). Fig. S3 shows typical TGA profiles of the dried sewage sludge, bio-oil, and solid residue.