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Thermochemical liquefaction characteristics of sewage sludge in different organic solvents

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ABSTRACT

Thermochemical liquefaction characteristics of sewage sludge in different organic solvents (methanol, ethanol and acetone) were comparatively investigated. Experiments were carried out in an autoclave at different temperatures ranging from 260 °C to 380 °C with a fixed solid/liquid ratio. The efficiency of above solvents in terms of conversion rate was found to be: methanol > ethanol > acetone. However, higher bio-oil yield was obtained with acetone as liquefaction solvent. The chemical properties of the bio-oil products were also significantly affected by the type of liquefaction solvent. Methanol and ethanol yielded mainly ester compounds, while acetone favored the formation of ketone and N-containing compounds. Meanwhile, some phenolic compounds, alcohols and very few hydrocarbons were also qualified. The calorific values of the bio-oils produced using methanol and ethanol were as high as 37.69 MJ/kg and 38.42 MJ/kg, respectively, much higher than that using acetone (26.74 MJ/kg). The results of thermogravimetric analysis (TGA) showed that the bio-oils contained a considerable amount of light components. And the content of low-boiling-point (bp < 350 °C) compounds ranged from 78.13% to 85.76% of the weight for above three bio-oils. On the whole, ethanol seems to be more suitable for sewage sludge liquefaction from the viewpoint of efficiency and renewability.

1. Introduction

Sewage sludge is the residue produced by the domestic or industrial wastewater treatment plants [1]. Sewage sludge is considered as a very heterogeneous material and comprises a mixture of various compounds. Specifically, sewage sludge consists of six groups of components: (1) nontoxic organic carbon compounds, for a large part from biological origin, (2) nitrogen- and phosphorous-containing components, (3) toxic inorganic and organic pollutants, (4) pathogens and other microbiological pollutants, (5) inorganic compounds, such as silicates, aluminates, and calcium- and magnesium-containing compounds, and (6) water [2]. Sewage sludge is becoming a public issue due to the ever-increasing amount and risk to the environment [3,4].

Agricultural application, landfill and incineration are the most common ways to dispose sewage sludge [5]. However, theses traditional disposal routes are facing increasing challenges due to land limitations and stringent regulations [6,7]. Thus it is necessary to develop alternative and sustainable disposal routes which could combine material recycling and sewage sludge disposal at the same time [8]. Sewage sludge is rich in volatile matter and thereby recognized as a potential bioresource for heating or perhaps as liquid fuel and chemicals [9]. The thermal technologies, such as gasification, combustion, liquefaction and pyrolysis, which have the advantages of recovering energy while disposing the sewage sludge, are gaining more and more attention on resource utilization of sewage sludge [5,9–12].

Liquefaction is a low temperature and high pressure thermochemical process during which biomass is converted into oily compounds (bio-oil) in water or other suitable solvents [13]. The products of biomass liquefaction are determined by various factors, including substrate type, heating conditions, solvent type, reactor configuration and catalyst [14]. Solvents, according to their polarity, can be classified into three categories: polar protic, dipolar aprotic and non-polar solvents. Polar protic solvents such as water and alcohols refer to compounds with a hydrogen atom attached to an electronegative atom like oxygen. Dipolar aprotic solvents such

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Table 1
Proximate and ultimate analysis of sewage sludge sample.

Proximate analysis (wt.%)[a]		Ultimate analysis (wt.%)[a]					HHV (MJ/kg)
Organic matters	Ash	C	H	N	S	O[b]	
60.8	39.2	31.29	3.83	4.84	3.43	17.41	14.57

[a] On a dry basis.
[b] O = 100 − (ash + C + H + N + S).

Table 2
Properties of selected liquefaction solvents [23,24].

Solvent	Formula	T_c (°C)	P_c (MPa)	ρ_c (g/cm^3)	Polarity[a]	Dielectric constant[b]
Water	H_2O	374	22.1	0.3320	100	79.7
Methanol	CH_4O	240	7.96	0.2720	76.2	32.6
Ethanol	C_2H_6O	243	6.39	0.2760	65.4	22.4
Acetone	C_3H_6O	235	4.8	0.2779	35.5	20.4

[a] Water taken as 100.
[b] Determined at 20 °C.

as acetone and 1,4-dioxane describe a molecule that does not contain an O—H bond. All solvents in this class contain a bond with a large bond dipole, which is a multiple bond between carbon and either oxygen or nitrogen. Non-polar solvents are compounds that have low dielectric constants and are not miscible with water (e.g., benzene and diethyl ether) [15].

So far, several investigations have been carried out on the liquefaction of sewage sludge in sub-/supercritical water [16–18]. However, the critical point of water (647.3 K, 22.1 MPa) means that the liquefaction process has to be operated in challenging conditions [19]. Besides, both the yield and the caloric value of bio-oil produced from biomass liquefaction using water as the reaction medium are relatively low [20,21]. Recently, organic solvents, such as ethanol, methanol, acetone, etc., have been utilized as the reaction medium instead of water to enhance the yield of bio-oil with lower oxygen content [14,19–21]. Li et al. [12] and Huang et al. [22] studied the liquefaction characteristics of sewage sludge in sub-/supercritical ethanol. There are rarely reports on the liquefaction of sewage sludge with different organic solvents as the reaction medium at identical conditions. Such work is significantly important to understand the effect of organic solvent type on the liquefaction characteristics of sewage sludge. Thus, it was felt to be of considerable value to fill this gap.

In this study, polar protic solvents (such as methanol and ethanol) and dipolar aprotic solvent (acetone) were adopted as liquefaction solvents. The effect of these solvents on the decomposition behaviors of sewage sludge was systemically studied in a high-pressure batch reactor at different temperatures. In addition, the elemental and chemical compositions of the produced bio-oil products were also analyzed. Meanwhile, the boiling point distributions of bio-oils were comparatively evaluated by the thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Materials

The raw biomass sample used in this work was secondary sewage sludge supplied from an urban wastewater treatment plant in Changsha City, Hunan Province (China). The biological treatment technology applied to the wastewater is improved oxidation ditch process. The produced excess sludge is concentrated and then mechanically dewatered without any stabilization treatment. The dewatered sludge as received was firstly dried in an oven at 105 °C for 24 h. Then the dried sludge solid was ground in a rotary cutting mill and screened into fractions of particle diameter 30–120 meshes. The resulting powder was stored in a jar at room temperature. The results of the proximate and ultimate analysis of the dried sludge powder are shown in Table 1.

All chemicals used in this study are of analytical reagent grade. The daily-diluted solutions were freshly prepared using deionized water. All glassware and plastic containers were washed with 15% nitric acid solutions and rinsed thoroughly with deionized water. Properties of the selected liquefaction solvents (methanol, ethanol, and acetone) and their critical constants are given in Table 2 [23,24]. Methanol, ethanol and acetone were individually used as liquefaction solvents in the experiments.

2.2. Liquefaction apparatus and procedure

Liquefaction experiments were conducted in a 500 mL autoclave (GSHA-0.5, China) at specified reaction temperature (260–380 °C). The vessel picture and schematic diagram of the reactor were shown in our previous work [22]. In each test, equal amounts of sewage sludge was mixed with 100 mL of solvent (methanol/ethanol/acetone) and fed into the reactor. Then, the reactor was sealed and heated from ambient temperature to the required temperature where it was maintained for 20 min. The temperature inside the reactor was monitored using an inner thermocouple and controlled by a proportional integral derivative module. The reactants were agitated vertically using a stirrer (60 rpm). After the treatment, an electric fan and cool water were used to cool the reactor to room temperature. Heating time was about 50–60 min and 1 h would be taken to cool the reactor to room temperature. The final reaction pressures for methanol, ethanol and acetone runs were 7.8–12.6 MPa, 6.1–10.7 MPa and 5.0–7.5 MPa, respectively.

2.3. Separation procedure

Fig. 1 depicts the details of the procedure for separating liquefaction products. Once the autoclave was cooled to room temperature, the gas products were vented in a fume hood. The gas products were not analyzed in this work since our main interest is in the liquid products. Furthermore, from a thermodynamics point of view, the gasification process normally leads to similar gas compositions containing CH_4, CO_2, CO and H_2 [15]. The solid/liquid products were rinsed from the autoclave by washing with ethyl acetate. The resulted suspension was filtered through a pre-weighed filter paper under vacuum, and meanwhile ethyl acetate was added to wash the remaining solid on the filter paper. The final remaining solid products were defined as liquefaction char (LC). This fraction was dried in an oven at 105 °C overnight and quantified to calculate the conversion rate. The filtrate was evaporated under reduced pressure at 50 °C to remove the solvents (liquefaction solvent and ethyl