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Interaction between sewage sludge components lignin (phenol) and proteins (alanine) in supercritical water gasification

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ABSTRACT

Abstract: The interaction between lignin and proteins was investigated to improve understanding of supercritical water gasification (SCWG) of sewage sludge from water treatment. Phenol and alanine were used as model compounds, and mixed in proportions from 0 to 100%. The mixtures were gasified at 400 °C and 22–26 MPa in a batch reactor with a residence time of 30 min. SCWG of the mixtures enhanced total gas, H_2, and CO_2 yields compared with weighted average values. The maximum increase of H_2 yield was at 60 wt% alanine, and the H_2 yield was about twice the weighted average value. Co-gasification of the compounds in supercritical water facilitated the removal of total organic carbon and total nitrogen from the aqueous phase, and the generation of oil phase products, mainly phenol compounds and organic compounds containing nitrogen. The increase of gas and oil phase products may be caused by phenol promoting the decomposition of alanine, while alanine promotes the condensation of phenol.

Introduction

Traditional energy sources such as fossil fuels are becoming scarcer, and their use is associated with environmental pollution, which has encouraged the development of new renewable energy technologies. One of these is the recovery of energy from biomass by supercritical water gasification (SCWG). SCWG of sewage sludge to produce hydrogen [1,2] is a promising method of using the biomass energy, because it not only solves the problem of sludge treatment, but also makes better use of wastewater treatment plants by turning waste into energy. Sewage sludge is a complex mixture, containing water, organic components, and inorganic salts. The organic components typically include proteins (18–40%), lignin

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(23–29%), lipids (6–19%), and carbohydrates (10–15%) [3–6]. These organic components may interact with each other and influence the reactions in SCWG, thereby affecting the yield and components of the final products.

To facilitate a better understanding of the reactions in SCWG, model compounds (glucose, amino acids) are often used to substitute for actual biomass [7–11]. However, a single type of model compound cannot completely simulate the complexity of biomass composition. A substantial amount of researches have been done on gasification of mixed model compounds in supercritical water (SCW). Goodwin et al. [12] used xylose and phenol as models for hemicellulose and lignin, respectively. They gasified xylose and xylose-phenol mixtures at 750 °C and 250 bar and found that xylose promoted the apparent conversion rate of phenol. Yoshida et al. [13,14] examined the gasification of cellulose, xylan, and lignin mixtures in SCW at 350 °C and 25 MPa, and found that less gas was produced from the mixtures containing lignin. Weiss-Hortala et al. [15] also confirmed that if phenol was present, the gasification efficiency of glucose was dramatically reduced, while Castello et al. [16] found that during SCWG of glucose/phenol mixtures, phenol mostly behaved as an inert component in terms of total gas production, although it played an inhibitory role towards H_2. Azadi et al. [17] carried out experiments on SCWG of glucose, glycine, glycerol, lauric acid, and humic acid (containing phenolic (Ar–OH) groups and similar to lignin), representing carbohydrates, proteins, alcohols, fatty acids, and humic substances in sludge, respectively. Investigating the effects of Raney nickel on the interaction between these model compounds, they found that at 0.1 g catalyst/g feed loadings, the presence of humic acid had a negative effect on gas production. Kruse et al. [18] reported a reduction in the glucose gasification efficiency in the presence of alanine with the addition of 0.2% $KHCO_3$. Similarly, L-proline caused significant reduction in the gasification efficiency of glycerol in SCW [19]. It is therefore well established that lignin and proteins may have some effects on SCWG of organic compounds. Because lignin and proteins are major constituents of sludge, the two substances will inevitably influence each other in SCWG. Therefore, it is important to elaborate on the behavior of the mixtures of the two substances in SCW to understand reaction pathways and improve technology for SCWG of sludge.

Lignin is a complex substance with aromatic rings, containing many Ar–OH groups. The main hydrolysis products of lignin are phenolic compounds [20], and because the main compounds in the liquid products from SCWG of guaiacol, a lignin model compound, were phenol and *o*-cresol [21,22], phenol was selected as a model compound to represent woody plant material [9]. Jarde et al. [23] found that sludge mainly comprises lignin-derived, lipid-derived, and nitrogenous compounds, which means that there are many Ar–OH groups in sludge, and that phenol can be used to simulate the lignin component of sludge. It is common to use amino acids as model compounds for proteins, and a simple amino acid, alanine, is generally preferred to simulate proteins [8,18,19] in SCW.

In this paper, we used phenol and alanine as model compounds for lignin and proteins, respectively, and gasified the pure compounds and various mixtures in SCW to explore the interaction between the two compounds to enhance understanding of the SCWG of sludge. Because operating at lower temperatures can decrease the capital and operating costs of a future industrial implementation, we carried out the experiments at 400 °C and 22–26 MPa in a batch reactor with a residence time of 30 min.

Experimental section

Materials

Phenol (Chinasun Specialty Products Co. Ltd., Changsu, China.) and alanine (Aladdin Industrial Corporation, Shanghai, China.) were pure reagents (99.5%). Distilled water was used throughout.

Apparatus and methods

The apparatus used in the experiments was as reported by Xu et al. [24] In each case, a total of 2.1 g of feed and 40 g of distilled water (5 wt%) were weighed into the reactor under an operating temperature of 400 °C, and pressure ranging from 22 to 26 MPa for a reaction time of 30 min. After the reaction, the reactors were fan cooled to room temperature and the products were recovered and separated according to the procedures outlined in Fig. 1. The gas products (GP) from the experiment were sampled using a syringe (20 mL) with a three-way valve for compositional analysis, and the rest of the gas volume was measured through the amount of saturated sodium hydrogen carbonate displaced. The remaining solid–liquid mixture (M) was centrifuged and filtered under vacuum through a slow filter paper to give aqueous phase products (AP). The residue remaining on the filter paper was combined with the residue from the reactor (R) and collected into a beaker; with the walls of the reactor and centrifuge tube being rinsed with ethanol/ethyl acetate (3:1) eluent (E). The combined residues were shaken in the eluent and filtered to check for insoluble solid products (SP) but the amount was too small to be measured. The filtrate containing (E) and E-soluble oils was collected into a pre-weighed flask and evaporated under reduced pressure at 60 °C, to obtain oil phase products(OP).

Gas products, such as H_2, CO, CO_2, CH_4, and other light organic gases (for example ethylene (C_2H_4) and ethane (C_2H_6)) were measured by gas chromatography (see Ref. [20]). N_2 was measured using a TCD detector with H_2 as the carrier gas under the same test conditions as for H_2.

Total organic carbon (TOC) and total phenol concentrations in LP were measured (see Ref. [20]). The amounts of ammonia nitrogen (NH_4^+-N) and total nitrogen (TN) were determined colorimetrically by ultraviolet–visible spectrometry using standard methods. [25] Residual phenol concentrations were measured by an Agilent 1260 Infinity liquid chromatograph equipped with a high-performance liquid chromatography (HPLC) pump, a C18 column, and an ultraviolet detector. The mobile phase was a 50:50 mixture of methanol and water, the column temperature was held constant at 30 °C and products were detected at a wave length of 270 nm.