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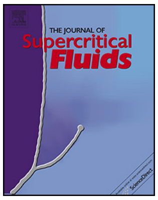

Subcritical and supercritical water gasification of humic acid as a model compound of humic substances in sewage sludge

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ABSTRACT

Humic acid is a model compound of sewage sludge that occurs as a result of decomposing organic matter in wastewater. In this study, humic acid gasification was performed at variable subcritical and supercritical water temperatures (325–600 °C), feed concentration (10–25 wt%) and reaction time (30–90 min). High H_2 yield of 0.79 mol/kg was obtained at 600 °C, 15 wt% humic acid and 75 min without any catalyst. Catalysts such as K_2CO_3, $Ni/Al_2O_3{-}SiO_2$, $FeCl_3$ and $ZnCl_2$ were examined to enhance H_2 production and humic acid degradation. While H_2 yield increased exponentially with rising $FeCl_3$ loading, $Ni/Al_2O_3{-}SiO_2$ and K_2CO_3 reduced H_2 yield due to bimolecular condensation and catalyst deactivation. Maximum yield of H_2 (4.09 mol/kg) and total gases (6.20 mol/kg) were obtained with 15 wt% humic acid and 15 wt% $FeCl_3$ at 600 °C and 75 min. Elevated temperatures and high $FeCl_3$loading promoted the degradation of humic acid with higher gas yields and fragmented surface morphology in char residues.

1. Introduction

Humic substances are the bulk organic constituents of humus found in soil, peat and coal. Humic acid and fulvic acid are the common types of humic substances that occur in soil, lakes, ocean water and sewage sludge as a result of biodegradation of organic matter [1]. Sewage sludge, a residual semi-solid byproduct of wastewater treatment plants, contains significant amount of decaying organic matter (e.g., carbohydrates, fats, proteins, organic acids, etc.), microorganisms, heavy metals and micro-pollutants (e.g., sterols, hormones and pharmaceutical residues) [2]. Sewage sludge originates from domestic, industrial, agronomic and other liquid-waste effluent streams. It has a high potential for use in the bioenergy sector due to its high organic matter content, approximately 50% on a dry basis [3].

Owing to its semi-solid nature (i.e. high water content), hydrothermal gasification of sewage sludge is considered an economically and environmentally promising technology. Supercritical water gasification (SCWG) reduces costs of expensive pre-drying processes of sewage sludge and can transform organics to H_2-rich syngas [3–5]. However, sewage sludge has a complex organic composition due to its heterogeneous ingredients including carbohydrates, crude fats, proteins, lignin and humic substances. The composition of sewage sludge and the concentration of its individual components vary greatly depending on wastewater sources and the sewage treatment process, which make it challenging to understand the reaction pathways involved in its gasification in supercritical water (SCW) [6]. In order to address this issue, it is crucial to investigate the reaction mechanisms for each organic component in the sewage sludge.

The humic substances are the main refractory organics occurring in sewage sludge that include humic acids and fulvic acids [7]. Humic acid comprises over 80% of humic substance in sewage sludge. Its structure is more aromatic and less aliphatic compared to fulvic acid [8]. On the other hand, fulvic acids are lower molecular weight humic acids with higher oxygen content, suggesting less energy value. The structure of humic acid extracted from sewage sludge contains a lot of aromatics, heterocyclics and alicyclics [9], which are difficult to be gasified in SCW [10]. High concentrations of humic acid and fulvic acid could also lead to impediments in gasification leading to reactor plugging, corrosion and tar formation, although there is little literature to determine the facts. Therefore, this study on hydrothermal gasification of humic acid could establish selected necessary grounds for better understanding of thermochemistry of sewage sludge gasification.

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Azadi et al. [11] used humic acid as a model compound of humic substances in activated sludge and investigated its catalytic SCW reforming at 380 °C for 15 min using Raney nickel catalyst. Their investigations were concerned on the interactions between humic acid and other model compounds. They suggested that humic acid was difficult to gasify due to its recalcitrant condensed structures. Low carbon conversion and low gas yields were also reported due to the condensed structures of humic acid [11]. The lignin-derivatives such as those of cinnamyl, guaiacyl and syringyl compounds constitute the basic structure of humic acid [9]. The aromatic, condensed and polymeric nature of these organic compounds render recalcitrance to humic acid. Due to its stable carbon content (i.e. resistant to microbial and thermal degradation), humic acid is used as a supplement in agriculture to enhance soil quality and surfactant to heavy metal remediation [12].

Gong et al. [13] studied supercritical water oxidation (SCWO) of fulvic acid and the influence of reaction parameters and oxidation ratio on its degradation. Fulvic acid was easily degraded through SCWO process with the total organic carbon removal efficiency approaching 98% at 600 °C and 420 s. Moreover, the oxidation coefficient had a positive effect on the degradation of fulvic acid. Similarly, Kim et al. [14] treated actual leachate containing humic acid and ammonia compounds by SCWO process, and found out that the optimal destructive condition of humic acid in the presence of air was 3 min at 380 °C. Fekete et al. [8] carried out a simulation experiment of humic acid and fulvic acid in hot thermal water, and proved that the reaction temperature played an important role in their degradation.

Due to the increased interest in the valorization of sewage sludge and lack of systematic findings on its conversion to clean energy, our study was intended towards the subcritical and supercritical water gasification of humic acid as its chief refractory model compound. The effects of reaction temperature, feed concentration, reaction time on the gas yields and composition were investigated to determine the optimal reaction condition for H_2 production. Moreover, alkali (K_2CO_3), metal ($Ni/Al_2O_3–SiO_2$) and chloride ($FeCl_3$ and $ZnCl_2$) catalysts, were employed to understand their impacts on humic acid gasification. Spectroscopic and structural characterizations of char residues obtained at different temperatures and catalyst concentrations were performed to understand the thermal decomposition behavior during hydrothermal gasification.

2. Materials and methods

2.1. Materials

Humic acid was used as a model compound of humic substances present in sewage sludge for hydrothermal gasification. Homogeneous catalysts such as K_2CO_3, $ZnCl_2$ and $FeCl_3$ as well as heterogeneous commercial catalyst e.g. reduced $Ni/Al_2O_3–SiO_2$ (~65 wt% nickel) were used to examine their impacts on total gas yields and product gas composition. All the catalysts and humic acid were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). The proximate (volatile matter and ash) and ultimate (CHNS) analyses of humic acid are presented in Table 1. The volatile matter and ash contents in humic acid and chars were determined using ASTM D3175-11 and ASTM D3174-11 protocols, respectively.

2.2. Hydrothermal gasification reactor

The gasification experiments were performed in a stainless steel tubular fixed-bed batch reactor (12.7 mm outer diameter, 9.4 mm inner diameter and 406 mm length). The reactor schematic is shown in Fig. 1. The gasification assembly consisted of a temperature controller, a relief valve, a pressure gauge, a thermocouple, an electric heater, a tubular batch reactor, a 2 μm filter, a gas-liquid separator, a moisture trap and other accessory valves and tube connectors. All the stainless steel (SS316) tubings, fittings and valves used in the assembly were purchased from Swagelok® (Swagelok Central Ontario, Mississauga, ON, Canada).

Prior to the experiment, the reactor was vacuumed and purged with N_2 several times to remove air. N_2 was also used as an inert gas for pressurizing the reactor between 2.0 and 14.5 MPa, depending on the desired gasification temperature. The reactor was heated by an ATS Series 3210 furnace (Applied Test Systems, Butler, PA, USA) with a heating rate of 30 °C/min. After reaching the desired temperature, the reactor was maintained for desired reaction time. The condensed gasification products (i.e. liquid and gases) were separated using a gas-liquid separator. Moisture-free gas products were collected in Tedlar® bags (Environmental Sampling Supply, San Leandro, CA, USA) after passing through the moisture trap (Praxair Canada Inc., Mississauga, ON, Canada).

2.3. Gasification parameters

Hydrothermal gasification of humic acid was performed at ~24 MPa to explore the impacts of temperature, feed concentration, reaction time and catalyst concentration. Six different temperatures in the range of subcritical water (325 and 350 °C) and supercritical water (375, 400, 500 and 600 °C) were studied to determine their impacts on gas yield and composition. The feed concentration was varied from 10 to 25 wt% of humic acid to understand its conversion to gases. In a typical experiment, calculated amount of humic acid (e.g., 1.1 g at 10 wt%) was loaded into the reactor along with 9 mL of distilled water. After identifying the optimal temperature and feed concentration, the effect of different reaction times (30–90 min) was studied. The catalyst loading from 5 to 15 wt% such as K_2CO_3, $ZnCl_2$, $FeCl_3$ and $Ni/Al_2O_3–SiO_2$ was also examined for a comparative evaluation of catalyst effectiveness at an optimal temperature, feed concentration and reaction time.

2.4. Product analyses

The gas samples were analyzed using an Agilent 7820A gas chromatograph (Agilent Technologies, Santa Clara, CA, USA). Selected gaseous products (H_2, CO_2, CO, CH_4 and C_2H_6) were quantified. The gas chromatography system was equipped with a thermal conductivity detector (TCD), three packed columns and one capillary column. The carrier gas for the TCD detector was argon. While CO_2 was analyzed using Ultimetal Hayesep T 80/100 mesh column, H_2, CO and CH_4were analyzed using Ultimetal HayesepQ T 80/100 mesh column. N_2 and O_2 in the gas products were identified through Ultimetal molsieve13 80/100 mesh column. All the columns were maintained at 60 °C. The data were analyzed using Agilent Open LAB CDS ChemStation software.

Fourier transform infrared (FTIR) spectroscopy of raw humic acid and its chars generated at different temperatures and catalyst loadings was performed using a Bruker Alpha FTIR spectrometer (Bruker Optics Ltd, Milton, ON, Canada) to assay the organic functional groups. The acquired spectra averaged 64 scans collected from 500 to 4000 cm^{-1} (2 cm^{-1} resolution). Scanning electron microscopy (SEM) was also performed for raw humic acid and its chars to visualize the structural disintegration as a result of temperature and catalyst loading. SEM analysis was performed in a FEI Quanta 3D FEG DualBeam microscope (FEI Company, Hillsboro, OR, USA) operated at 20 kV under high vacuum condition. Denton Desk V Sputter coater (Denton Vacuum, Moorestown, NJ, USA) was used for gold coating the samples before imaging.

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