

Hydrothermal gasification of humic acid as a model compound of sewage sludge for hydrogen rich-syngas production

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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 H₂ yield of 0.79 mol/kg was obtained at 600°C, 15 wt% humic acid and 75 min without any catalyst. Catalysts such as K₂CO₃, Ni/Al₂O₃-SiO₂, FeCl₃ and ZnCl₂ were examined to enhance H₂ production and humic acid degradation. While H₂ yield increased exponentially with rising FeCl₃ loading, Ni/Al₂O₃-SiO₂ and K₂CO₃ reduced H₂ yield due to bimolecular condensation and catalyst deactivation. Maximum yield of H₂ (4.09 mol/kg) and total gases (6.20 mol/kg) were obtained with 15 wt% humic acid and 15 wt% FeCl₃ at 600°C and 75 min.

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, microorganisms, heavy metals and micro-pollutants [2]. Owing to its semi-solid nature (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 H₂-rich syngas [3-5]. However, the composition of sewage sludge and the concentration of its individual components vary greatly depending on wastewater sources and the sewage treatment process, which makes 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]. 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.

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 (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 in 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 sub- and super-critical 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 H₂ production. Moreover, alkali (K₂CO₃), metal (Ni/Al₂O₃-SiO₂) and chloride (FeCl₃ and ZnCl₂) catalysts, were employed to understand their impacts on humic acid gasification.

MATERIALS AND METHODS

Humic acid was used as a model compound of humic substances present in sewage sludge for hydrothermal gasification. Homogeneous catalysts such as K₂CO₃, ZnCl₂ and FeCl₃ as well as heterogeneous commercial catalyst e.g. reduced Ni/Al₂O₃-SiO₂ (~65 wt% nickel) were used to examine their impacts on total gas yields and product gas composition. Humic acid contained 25.6 wt% ash and 74.4% volatile matter. The carbon, hydrogen, nitrogen and oxygen concentrations in humic acid were 45 wt%, 2.2 wt%, 1.9 wt% and 25.2 wt%. The heating value of humic acid was

14.3 MJ/kg.

The gasification experiments were performed in a stainless steel tubular fixed-bed batch reactor. The schematic of the reactor was present in our previous paper along with the experimental procedures, sample collection and separation [15].

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 to 90 min) was studied. The catalyst loading from 5-15 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.

RESULTS AND DISCUSSION

The effects of reaction temperature on the gas yield and composition are shown in Fig. 1. The components of the gaseous products of humic acid gasification were mainly H_2 and CO_2 with small amounts of CH_4 and C_2H_6 . The levels of CO were found either in traces or negligible amounts. It should be noted that no CO yields in the gas products were detected.

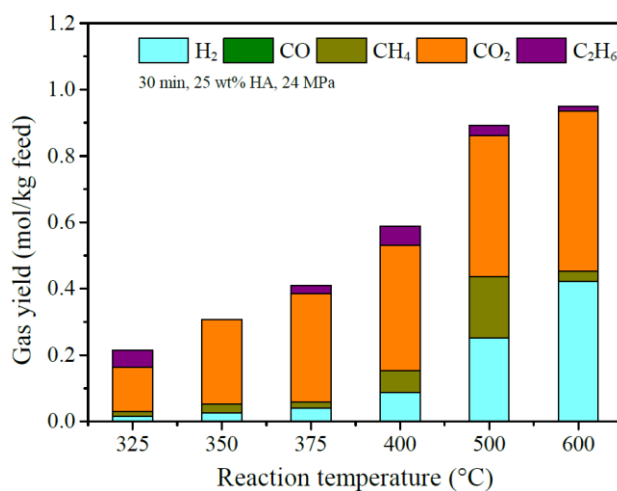


Figure 1. Effect of reaction temperature on gas yield and composition

As the temperature increased, humic acid (25 wt% feed concentration) showed an increase in the H_2 yields from 0.02 mol/kg (at 325°C) to 0.42 mol/kg (at 600°C). The total gas yields also increased from 0.21 mol/kg to 0.95 mol/kg as the temperature increased from subcritical water (at 325°C) to supercritical water (at 600°C). At the subcritical temperatures (325-350°C), CO_2 was the main component of the gas product, accounting for more than 60% of the total gas yield. At supercritical temperatures (375-600°C), CO_2 yield was compensated by higher H_2 production. At

600°C, the H₂ yields increased by 26 times while the total gas yields increased by four times. Therefore, higher temperature can lead to producing H₂-rich syngas with the percentage of H₂ being increased from 7.3% to 44.4%. Higher supercritical water temperatures lead to reforming and water-gas shift reactions resulting in greater yields of H₂ and CO₂ [16].

Higher gasification temperatures result in alterations in the molecular structure of water leading to poor intra- and intermolecular hydrogen-bonding resulting in biomass decomposition [17]. Temperature above the critical point of water (~374 °C) results in the decrease of water density impeding the ionic product formation. As the ionic product formation is impacted, the free radical mechanism is favored resulting in higher gas yields [18]. Furthermore, high temperatures favor water-gas shift reaction resulting in higher yields of H₂ and CO₂ [19]. In this study, the CO produced was consumed in water-gas shift reaction to yield H₂ and CO₂.

After determining that the gasification temperature of 600°C is optimal for higher H₂ yields, the effects of different feed concentration ranging from 10 to 25 wt% were investigated for the gasification of humic acid at 600°C and 30 min (Fig. 2).

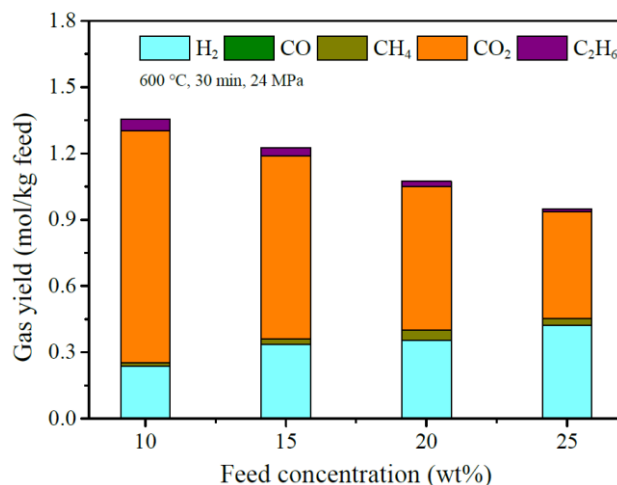


Figure 2. Effect of feed concentration on gas yield and composition

It is well-known that lower feed concentration can lead to higher gas yields due to ionic and free radical mechanisms of SCW [15]. It is noteworthy that the lower feed concentrations of humic acid in our SCWG experiments promoted the total gas yields but they did not improve the H₂ production. The total gas yield increased from 0.95 to 1.35 mol/kg when the feed concentration decreased from 25 to 10 wt% (Fig. 2). However, the H₂ yield reduced from 0.42 to 0.24 mol/kg. While the CO₂ yield increased significantly at lower feed concentration. However, the humic acid concentration of 15 wt% was selected as the optimal feed concentration because of its high H₂ content in the total gas product. The CO₂ yield increase at lower feed concentration is following the thermodynamics of reverse water-gas shift reaction [20]. The decrease in the yields of CO₂ at higher feed concentration was attributed to the lower occurrence of water-gas shift reaction at higher feed concentrations. The amount of water molecules decreases in biomass slurry with higher feed concentration resulting in lower reaction rates. The yield of CH₄ increased from 0.02 to 0.05 mol/kg with the rise in humic acid concentration. This could be due to the improved methanation reaction where CO₂ reacts with H₂ to generate CH₄ [16]. This supports our findings where CH₄

increases at higher feed concentration.

The impact of reaction time was further investigated after asserting the optimal temperature and feed concentration at 600°C and 15 wt%, respectively. As shown in Fig. 3, a rise in the total gas yield was observed as the reaction time prolonged. When reaction time increased from 30 to 90 min, the total gas yield increased from 1.23 to 1.71 mol/kg. In the same way, H₂ and CH₄ yields also increased from 0.34 to 0.74 mol/kg and from 0.03 to 0.21 mol/kg, respectively. The H₂ concentration in the gas products increased until the reaction time of 75 min (0.79 mol/kg) after which it decreased at 90 min (0.74 mol/kg). During the entire reaction durations, the CO₂ yield remained almost unchanged (0.66 to 0.83 mol/kg).

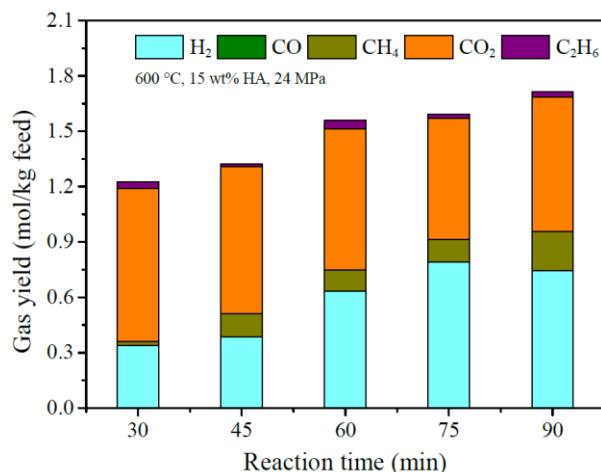


Figure 3. Effect of residence time on gas yield and composition

Longer reaction time improves CO₂ and CH₄ yields by promoting thermal cracking reactions at elevated temperatures [21]. Higher CH₄ levels result from secondary methanation reaction at longer reaction times [22]. As the reaction time is increased, the reforming reaction, watergas shift reaction and methanation reactions proceed more efficiently, thus enhancing the gas product yields [15, 16].

The above-mentioned observations indicate that satisfactory yield of H₂ (0.79 mol/kg) was obtained at 600°C using a humic acid concentration of 15 wt% and a reaction time of 75 min at 24 MPa pressure. In order to maximize the H₂ yields, four different catalysts were employed and their effects on the gas yields and composition are shown in Fig. 4. Compared to non-catalytic SCWG (1.59 mol/kg), the addition of K₂CO₃, Ni/Al₂O₃-SiO₂ and ZnCl₂ increased the total gas yields up to 1.64, 1.79 and 2.19 mol/kg, respectively. However, the concentration of H₂ in the gas products gradually decreased with their application, and ranged between 0.61 and 0.71 mol/kg. The condensed structure of humic acid and lack of reactive oxygen functional groups lead to lower carbon conversion and less gas yields even at high temperatures.

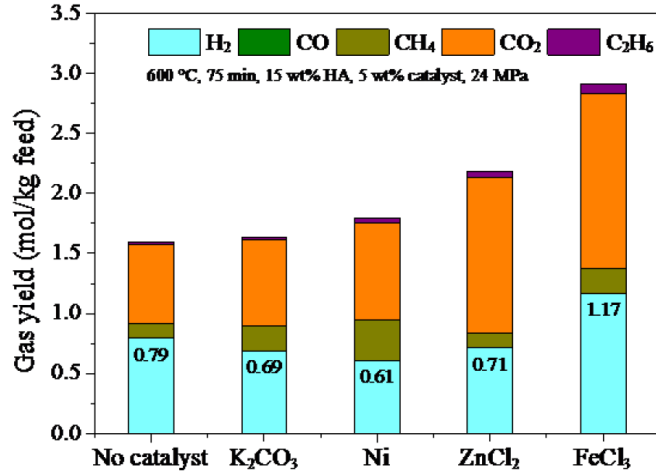


Figure 4. Effect of different catalysts on gas yield and composition

Although Ni/Al₂O₃–SiO₂ showed the lowest H₂ yield, it also resulted in the highest CH₄ yield. Extended reaction times along with nickel and ruthenium catalysts favor methanation reaction leading to reduced H₂ yields and increased CH₄ yields [23]. In our study, the addition of FeCl₃ significantly promoted H₂ (1.17 mol/kg) and total gas production (2.91 mol/kg) from humic acid. The catalytic effect of iron-based catalyst is considered similar to commercial alkali catalysts [24]. The addition of 5 wt% FeCl₃ increased the H₂ yield from 0.79 mol/kg (non-catalytic) to 1.17 mol/kg, indicating approximately 48% rise.

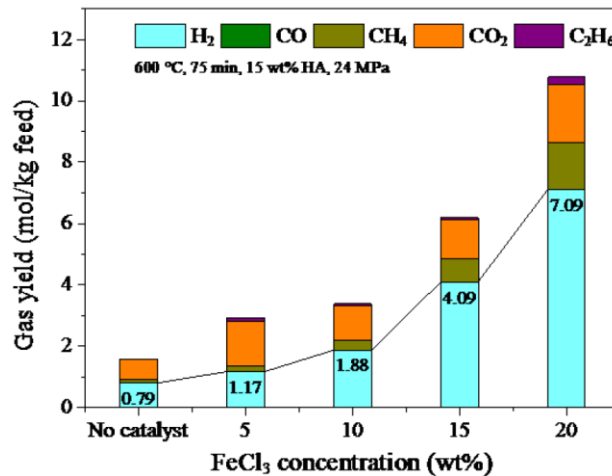


Figure 5. Effect of catalyst concentration on gas yield and composition

The effects of different FeCl₃ concentrations on gas yields and composition are shown in Fig. 5. The H₂ yields increased exponentially with rising FeCl₃ concentrations. With FeCl₃ concentration approaching 15 wt%, the H₂ yield increased to 4.09 mol/kg, which is approximately five times higher than non-catalytic SCWG of humic acid. Compared to 5 wt% FeCl₃, the CO₂ yield was lowered and CH₄ yield was considerably higher at 15 wt% FeCl₃. This was due to the catalytic hydrogenation of CO₂ to CH₄ via Sabatier reaction, which is also thermodynamically favored at higher temperatures [25].

CONCLUSIONS

The effects of reaction parameters and catalysts on gas yield and composition from subcritical and supercritical water gasification of humic acid were investigated for the first time. Higher supercritical water temperature (600°C), longer reaction time (75 min) and moderate feed concentration (15 wt%) were optimal for higher H₂ yield of 0.79 mol/kg. The reaction time of 90 min increased the total gas yields (1.71 mol/kg) by supplementing CH₄ yield (0.21 mol/kg) through methanation reaction and reducing H₂ yield (0.74 mol/kg). The application of 5 wt% catalysts including Ni/Al₂O₃-SiO₂, K₂CO₃ and ZnCl₂ resulted in higher total gas yields (from 1.64 to 2.19 mol/kg) than non-catalytic SCWG (1.59 mol/kg) but lacked the ability to enhance H₂ concentration. A decrease in H₂ yields (0.61 and 0.71 mol/kg) was observed with these catalysts addition due to the tendency of humic acid to shift the thermochemical mechanisms towards bimolecular condensation reactions leading to char and tar formation. The yields for H₂ and total gases increased exponentially with higher FeCl₃ loading. Maximum H₂ yield (4.09 mol/kg) and total gas yield (6.20 mol/kg) were obtained with 15 wt% of humic acid and 15 wt% FeCl₃ at 600°C and 75 min.

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