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# Catalytic gasification of dewatered sewage sludge in supercritical water: Influences of formic acid on hydrogen production

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## ABSTRACT

Promoting hydrogen production from supercritical water gasification of dewatered sewage sludge at low temperatures has become the essential to realization of technology resource utilization. Here we report supercritical water gasification of dewatered sewage sludge in a batch reactor. Total gas yield increased as the amount of formic acid increased, with hydrogen yield increasing significantly from 0.16 to 10.07 mol/(kg organic matter) as the formic acid increased from 0 to 6 wt%. The amount of undesired phenols in the liquid products was reduced and char in solid residue was also suppressed. An intermediate reaction was also conducted to investigate the mechanism by which formic acid promoted hydrogen production. Results indicated that formic acid acted as an acid hydrolysis agent and an effective hydrogenating agent that facilitated rapid hydrolysis of carbohydrates to produce small molecules and effectively suppressed polymerization. Overall, the method developed herein has the potential to promote hydrogen production by radical reaction.

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## Introduction

Dewatered sewage sludge (DSS) with a high moisture content is an inevitable product of wastewater treatment. Increased investment in the sewage treatment industry has led to increases in the amount of DSS with the construction and expansion of wastewater treatment plants. As a result, it is now necessary to develop methods to handle the large amount of DSS being generated.

Supercritical water gasification (SCWG) is regarded as an emerging economical and environmentally friendly technology

for sewage sludge treatment and hydrogen production. This method avoids expensive drying, and can transform the organic matter (OM) in DSS into clean energy sources such as hydrogen [1–3]. However, this low hydrogen production prevents the practical application of SCWG for energy recovery from DSS [4,5]. Consequently, it is necessary to develop a method for promotion of gasification reaction and to improve hydrogen production to enable the industrialization of this technology.

A number of processes have been investigated to improve hydrogen production, including the use of suitable additives as catalysts in SCWG, which can accelerate gasification reaction

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and allow low temperature gasification [6–8]. Commonly used catalysts include carbon, metals, metal oxides and alkalis. Activated carbon catalyst is mainly used to enhance the water–gas shift reaction to improve hydrogen production [9]. Xu et al. [10] investigated the gasification of sewage sludge with activated carbon catalysts in supercritical water and found that carbon could effectively increase hydrogen production and carbon conversion efficiency. However, effective catalytic effect required higher temperature ( $>700\text{ }^{\circ}\text{C}$ ), which could further increase operating costs. The use of Ni catalyst is efficient with high catalytic activity for  $\text{H}_2$  and functions by promoting steam reforming reaction [11,12]. Sawai et al. [13] reported that Ni catalyst improved hydrogen production in the SCWG of sewage sludge using a bench scale batch reactor. Gong et al. [14] also found that not only separate Ni catalyst but combined NaOH additive can effectively promoted hydrogen production from the SCWG of different sewage sludges. However, deposition of inorganic salts of DSS and char generated on the catalyst surface degrades catalytic effect. Alkali catalysts are widely used as homogeneous catalysts in hydrothermal gasification as they are not only cost effective but also can effectively promote water–gas shift reaction and improve hydrogen production [15–17]. Zhai et al. [18] found that  $\text{K}_2\text{CO}_3$  significantly improved gasification efficiency of the SCWG of digested sludge. Zhang et al. [19] also reported that NaOH catalyst had a positive effect on hydrogen production from the partial oxidative gasification of municipal sludge with NaOH catalyst. Xu et al. [20] investigated the catalytic effects of alkali salts (NaOH, KOH,  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}(\text{OH})_2$ ) on the SCWG of DSS and found that hydrogen yield increased and char content was suppressed in the presence of the alkali salts. Conversely, decreased solubility of inorganic compounds may result in precipitated salts causing plugging in the reactor.

In addition to the aforementioned problems, there are other issues regarding the heavy metals. Specifically, common metal or alkali metal catalysts may cause increased heavy metals content in the final products, resulting in product separation difficulties. Accordingly, if there is an organic additive, which can be dissolved in subcritical water at lower temperatures to promote gas production by rapid catalytic degradation of organic matter in the sludge, simultaneously avoiding sintering, plugging and product separation.

In recent years, the application of organic solvent formic acid (FA) as a reaction medium for hydrothermal hydrolysis of organic matter has been reported to give high conversion rates with good yields of small molecule compounds at low temperatures (50–350  $^{\circ}\text{C}$ ).

Watanabe et al. [21] reported that a high FA concentration and low temperature favored the formation of levulinic acid from glucose and hindered aldol polymerization. Yemiş et al. [22] found that FA could effectively catalyze conversion of xylose to furfural by microwave-assisted reaction. Onwudili [23] investigated the effects of FA on the composition of liquid products during two-stage hydrothermal conversion of alkali lignin in a batch reactor, and found that the mass fraction of liquid products reached up to 40% in the presence of FA. Zhang et al. [24] used FA as a catalyst to improve bio-crude production from pulp/paper-mill sludge via co-liquefaction in hot-compressed water, and found that FA enhanced the heavy oil yield at 300  $^{\circ}\text{C}$  and reduced the solid yield. The

results of these studies show that FA is an effective catalyst of organic matter decomposition.

It may also be possible for FA to be used as a suitable additive to enhance degradation of organic matter in sewage sludge under subcritical conditions, further to promote the gasification in supercritical water to generate hydrogen production. Furthermore, FA is one of the key intermediates during the SCWG of sludge, which makes it an interesting candidate for DSS hydrolysis. Although FA can effectively catalyze organic matter pyrolysis, it is not clear if it will promote rapid degradation of organic matter in the DSS under subcritical conditions and further gasification of hydrogen-rich gas.

In the present study, the SCWG of DSS with FA was investigated under the given reaction conditions to determine the influence of different amounts additive of FA to the products. Thereafter, variations in the products of the intermediate reaction process were analyzed, and a possible reaction mechanism was initially revealed to provide a preliminary understanding of the influence of FA on hydrogen production.

## Materials and methods

### Materials

In this work, the DSS was collected from WWTP in Jiangsu, China. The DSS sample was collected from the WWTPs and stored at a temperature below 4  $^{\circ}\text{C}$  until it was used in experiments. The compositions, in terms of the content of OM, moisture, and ash, metals, as well as ultimate analyses of DSS, are listed in Tables 1 and 2. Formic acid (88% in water) was analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd.

### Experimental apparatus and procedure

The SCWG of DSS was performed in a 316L stainless steel batch reactor obtained from the Songling Chemical Instrument Co., Yantai, Shandong, China. The schematic presentation of the reactor is shown in Fig. 1. The specific nature of the equipment and procedures as described in the literature [5].

Typically, 44.6 g of DSS (moisture content of 73.87 wt%) and 0–6 wt% (DSS) FA were placed in the reactor, which was then

**Table 1 – Properties of the dewatered sewage sludge tested.**

Moisture content (wt%)	Organic matter (wt%)	Ash (wt %)	pH	Ultimate analysis (wt%) <sup>a</sup>					HHV (MJ/kg) <sup>c</sup>
				C	H	N	S	O <sup>b</sup>	
73.87	26.18	70.12	7.6	12.98	2.12	1.93	1.01	4.24	4.78

<sup>a</sup> On an air-dried basis.

<sup>b</sup> By difference ( $\text{O}\% = 100\% - \text{ash}\% - \text{C}\% - \text{H}\% - \text{N}\% - \text{S}\%$ ).

<sup>c</sup> Higher heating value (HHV) calculated by the Dulong Formula, i.e.,  $\text{HHV (MJ/kg)} = 0.3393\text{C} + 1.443(\text{H} - \text{O}/8) + 0.0927\text{S} + 0.01494\text{N}$ .

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