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# Lewis acid catalyzed gasification of humic acid in supercritical water

Miao Gong[a,b], Sonil Nanda[b], Howard N. Hunter[c], Wei Zhu[d], Ajay K. Dalai[e], Janusz A. Kozinski[b,*]

[a] School of Civil Engineering, Hefei University of Technology, Hefei, Anhui, China
[b] Department of Earth and Space Science and Engineering, Lassonde School of Engineering, York University, Toronto, Ontario, Canada
[c] Department of Chemistry, York University, Toronto, Ontario, Canada
[d] College of Environment, Hohai University, Nanjing, Jiangsu, China
[e] Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

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ABSTRACT

Humic acid is a model compound of sewage sludge that occurs as a result of decomposing organic matter. Supercritical water gasification of humic acid was performed at a temperature, feed concentration and reaction time of 600 °C, 15 wt% and 75 min, respectively with variable concentrations (5–15 wt%) of Lewis acid metal chloride catalysts. The non-catalytic gasification of humic acid resulted in $H_2$ yield (0.79 mol/kg), total gas yield (1.59 mol/kg), carbon gasification efficiency (2.2%), $H_2$ gasification efficiency (10%) and lower heating value of 5.1 kJ/Nm$^3$. In contrast, 15 wt% of Lewis acid catalysts loading significantly improved $H_2$ yields (2.79–11.03 mol/kg), total gas yields (4.72–15.44 mol/kg), carbon gasification efficiency (5.7–12.4%), $H_2$ gasification efficiency (40.9–141.6%), energy recovery (8.8–33.79%) and lower heating value of gas products (22.4–72.3 kJ/Nm$^3$). The activity of Lewis acids was in the order: $CaCl_2 < ZnCl_2 < FeCl_3 < CuCl_2 < NiCl_2 < AlCl_3$. The addition of Lewis acid catalysts led to an increment in $H_2$ yield due to ring-opening reaction and intermediates gasification. High catalyst loading promoted the degradation of humic acid with greater gas yields and fragmented surface morphology of char residues. The liquid effluents from Lewis acid catalyzed gasification of humic acid contained considerable amounts of aromatic and aliphatic components.

## 1. Introduction

Humic acid is a common type of humic substance found in soil, peat, coal, lakes, ocean water and sewage sludge as a result of biodegradation of organic matter [1]. Typically, humic acid has the chemical formula $C_{187}H_{186}O_{89}N_9S$. It comprises about 80% of humic substance in sewage sludge. Due to its widely originating sources and heating value, humic acid can be considered as a useful organic component for energy generation. Owing to its high water content of sewage sludge, its gasification in supercritical water (SCW) could be an economically and environmentally-friendly technology. Supercritical water gasification (SCWG) can reduce the cost of expensive drying processes currently applied to sewage sludge and transform organics including humic acid to syngas [2–4].

Humic acid typically contains heterocyclic compounds such as carboxylic, phenolic, alcoholic and carbonyl fractions with high molecular weight [5,6], which are difficult to be gasified in SCW [7]. Azadi et al. [8] investigated the catalytic SCW reforming of humic acid as a model compound of humic substances in activated sludge at 380 °C for 15 min using Raney nickel catalyst. From their study 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. Lower conversion of carbon with compromised gas yields was also reported due to the condensed structures of humic acid. The low $H_2$ production from the hydrothermal gasification of humic acid prevents its practical application in SCWG for energy recovery. Therefore, significant research advancements are necessary to promote the gasification reactions and improve $H_2$ production from humic acid and its precursor sewage sludge.

Suitable catalysts (e.g., Ni and KOH) in SCWG can accelerate the gasification reaction even at low temperatures of 400–450 °C [9,10], which can promote $H_2$ production and reduce the operating costs.

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[*] Corresponding author at: Lassonde School of Engineering, York University, Toronto, Ontario, M3J 1P3, Canada.
*E-mail address:* janusz.kozinski@lassonde.yorku.ca (J.A. Kozinski).

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However, humic acid has been found to deactivate specific catalysts such as nickel by promoting bimolecular condensation reactions [8]. The biomolecular reactions are the non-desired secondary reactions that limit the carbon conversion rate through the formation of stable compounds such as tars and char. Humic acid has a chemical structure analogous to lignin. The lignin-derivatives such as cinnamyl, guaiacyl and syringyl compounds also constitute the basic backbone of humic acid [6]. Similar to lignin, these components render recalcitrance to humic acid and lower its degradation rate even at extreme thermochemical conditions.

Lewis acids have been found to be quite effective in lignin degradation and promoted gas production. Davoudzadeh et al. [11] studied the degradation of kraft lignin at temperatures of 110–300 °C using $AlCl_3$ and $BF_3$. A maximum yield of 25% of distillable products was obtained under low-pressure conditions. Sugita et al. [12] studied the hydrogenolysis of kraft lignin with tetralin at 400–420 °C, using $FeCl_3$ and $ZnCl_2$ as Lewis acid catalysts. The liquid product mixture consisted of mainly phenols and cresols with the highest yields of 24 wt% reportedly obtained with $FeCl_3$. Hepditch et al. [13] investigated the degeneration of Alcell-derived lignin in a batch reactor by using Lewis acid catalysts such as $NiCl_2$ and $FeCl_3$. The highest conversions of 30% and 26% with $NiCl_2$ and $FeCl_3$, respectively were obtained at 305 °C in one hour.

Shu et al. [14] reported that the Lewis acid $CrCl_3$ showed an outstanding hydrogenolysis effect when combined with Pd/C on the catalytic hydrogenolysis of alkali lignin. Moreover, the products could be regulated efficiently through the modification of the metal cation of $MCl_x$ due to the acid catalysis and coordination catalysis mechanism. The Lewis acid catalyst $CrCl_3$ not only promotes lignin hydrogenolysis but also favors depolymerization of lignin [15]. Güvenatam et al. [16,17] investigated the catalytic effects of different Lewis acid catalysts on depolymerization of Protobind lignin and soda lignin in a mixture of ethanol and water at 400 °C. They found that Lewis acid metal chlorides highly promote the depolymerization of lignin in supercritical ethanol by catalyzed dehydration, oligomerization and hydrogen-transfer reactions. Furthermore, Lewis acid has been found to efficiently convert glucose and other carbohydrates to produce 5-hydroxymethylfurfural [18,19], which is a versatile intermediate for the production of biofuels and industrially relevant value-added chemicals. Schwiderski and Kruse [20] studied the effects of Lewis acid $AlCl_3$ on the glycolaldehyde conversion and found that it catalyzes ketol-endiol tautomerism, dehydration, retro-aldol reaction and benzilic-acid rearrangement.

To the best of our knowledge, there is less literature available on SCWG of humic acid to produce syngas. In addition, there is no study reported so far on the hydrothermal conversion of humic acid using Lewis acids as catalysts. Therefore, it remains uncertain as whether Lewis acids can accelerate the degradation of humic acid and promote syngas production. Due to the facts that humic acid and lignin have similar chemical structures, and Lewis acid can efficiently degrade lignin, we objectified our work to examine the behaviors of different Lewis acid metal chlorides in SCW during humic acid conversion. The main interest of this work was to study the catalytic effects of different Lewis acid catalysts on $H_2$ production from SCWG of humic acid (at 600 °C, 75 min and 24 MPa). Physico-chemical, spectroscopic and structural characterizations of humic acid char residues obtained with different Lewis acid catalysts were performed to understand the thermal decomposition behavior of humic acid during SCWG. The liquid effluents from each catalytic gasification experiment were also assayed using spectroscopic techniques to determine the intermediate degradation products.

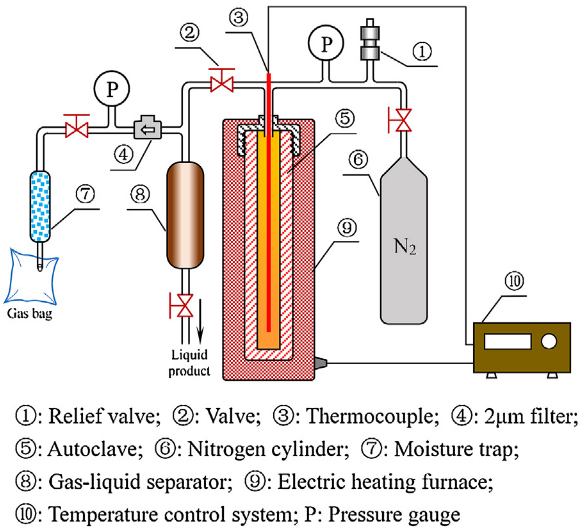

**Fig. 1.** Schematic of the tubular batch reactor for supercritical water gasification.

## 2. Materials and methods

### 2.1. Feedstock and catalysts

Humic acid and different Lewis acid metal chloride catalysts (e.g. $AlCl_3$, $CaCl_2$, $CuCl_2$, $FeCl_3$, $NiCl_2$ and $ZnCl_2$) were purchased from Sigma-Aldrich (Oakville, ON, Canada). The ultimate analysis (carbon, hydrogen, nitrogen and sulfur: CHNS) of humic acid and chars was performed using an Elementar Vario EL III CHNS analyzer (Elementar Analysensysteme, Hanau, Germany). The higher heating value (HHV) of humic acid and its chars was calculated using the modified Dulong's formula (Eq. (1)).

$$\mathrm{HHV(MJ/kg)} = (0.3393 \times \mathrm{Cwt\%}) + [1.443 \times (\mathrm{Hwt\%} - \mathrm{Owt\%}/8)] + (0.01494 \times \mathrm{Nwt\%}) \tag{1}$$

### 2.2. Hydrothermal gasification apparatus

The SCWG of humic acid was performed in an SS316 tubular fixed-bed batch reactor (outer diameter: 12.7 mm, inner diameter: 9.4 mm and length: 406 mm). The schematic of the reactor is shown in Fig. 1. The SCWG set-up consisted of the tubular reactor, temperature controller, thermocouple, electric heater furnace, relief valve, pressure gauge, 2 μm filter, gas-liquid separator, moisture trap and other accessory valves and fittings. The tubes, valves, connectors, fittings are other accessories were made of stainless steel (SS316) and purchased from Swagelok® (Swagelok Central Ontario, Mississauga, ON, Canada).

### 2.3. Lewis acid catalyzed humic acid gasification

To comprehensively study the effects of Lewis acid catalysts on humic acid gasification, the conditions such as temperature, pressure, reaction time and feed concentration of humic acid was kept constant. The SCWG of humic acid was performed at a temperature of 600 °C, pressure of 24 MPa and 75 min of reaction time. The feed concentration of humic acid selected for all experiments was 15 wt%. In a typical experiment, 1.59 g of humic acid with and without catalyst was loaded into the tubular fixed-bed reactor along with 9 mL of distilled water. The Lewis acid metal chloride catalysts

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