Low-temperature catalytic gasification of sewage sludge-derived volatiles to produce clean H₂-rich syngas over a nickel loaded on lignite char

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Abstract

Catalytic gasification (CG) of sewage sludge-derived volatiles (SSDVs) was investigated over a prepared nickel loaded on Loy Yong lignite char (Ni/LYLC) in a two-stage fixed-bed reactor to understand the effects of the catalyst, temperature, and steam on the gas yields and nitrogen transformations. Non-catalytic thermal decomposition of SSDVs below 650 °C is not effective for decomposing the tar and converting the volatile nitrogen species (VNSs) to N₂. Ni/LYLC proved to be quite active not only for tar reduction, but also for the conversion of VNSs to N₂ at 650 °C. CG of SSDVs over Ni/LYLC produced significant amount of clean H₂-rich syngas. CG above 650 °C results in the increase of nickel crystallite size and the deactivation of Ni/LYLC for tar decomposition. The study revealed the possibility of using Ni/LYLC as a potential catalyst for low-temperature CG of sewage sludge to produce clean H₂-rich syngas.

Keywords: Sewage sludge; Catalytic gasification; Nickel loaded on lignite char; H₂-rich syngas; Nitrogen transformation

1. Introduction

Agricultural application, landfill, and incineration are the most common disposal processes for sewage sludge (SS), whereas the traditional disposal routes are becoming more and more unacceptable due to land limitations and stringent regulations. Alternatively, using SS as a biomass resource for energy production is regarded as an environmentally acceptable disposal route with

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potential financial benefits. Several thermochemical conversion technologies, including pyrolysis, gasification, and liquefaction, are currently under development [1,2]. Among these processes, gasification is effective for converting SS to syngas or H₂-rich gas, which can be used as a fuel to generate electricity and heat or as raw material for chemical synthesis [3]. It is also advanced in reducing waste volume, removing toxic organic compounds, and fixing heavy metals in the resulting solid [4].

However, tar produced during gasification is one of the problems to be solved. Tar is a complex mixture of condensable alkanes, arenes, and heteroatom-containing species. It can condense on pipes and filters and may cause blockage and corrosion during combustion in the engines and turbines [3]. Many attempts, e.g., optimizing gasification conditions and gasifier design, thermal cracking, and catalytic gasification (CG), have been tried to remove tar from SS gasification [3,5]. Among the techniques, CG is regarded as one of the promising techniques for tar removal under moderate conditions. Dolomite was reported to be quite active for the decomposition of tar, which was derived from air and air-steam gasification of SS, at 800 °C [3,6], but it is easily eroded as a soft and fragile material, limiting its use in some types of reactors such as in a fluidized-bed reactor [7]. Olivine, alumina, zeolite, and activated carbon are also active for tar decomposition from high temperature gasification of SS [8,9]. Since the high ash yield in SS causes the slagging and fouling in thermal conversion systems when a gasifier is operated at high temperatures [10], it is essential to develop low-temperature SS gasification technology.

Besides, nitrogen content in SS is higher than that in woody biomass. The nitrogen-containing species (NCSs) in SS are converted to NH₃, HCN, and nitrogen in tar (N_{tar}) during pyrolysis and then converted to NO_x and N₂O during gasification and combustion, causing significant environmental pollution [11-13]. It is of great significant to understand the releasing behaviors of NCSs and their transformation during pyrolysis and gasification and reducing the emission of NO_x precursors is important for clean H₂ and syngas production. Many researchers investigated the formation and distribution of NCSs from pyrolysis and gasification of coals and biomass [7], but

few reports were issued on the catalytic decomposition of NCSs during SS gasification.

Nickel-based catalysts proved to be quite active not only for tar reduction, but also for NH₃ decomposition, even at 600 °C [7]. Nevertheless, commercial nickel-based catalysts are expensive. It is economically infeasible using high cost catalysts for SS gasification. We prepared a cost-effective and active nickel loaded on Loy Yong lignite char (Ni/LYLC) via ion-exchange. The catalyst has been successfully utilized for tar reforming in woody biomass gasification [14], but has not been applied to the CG of biomass wastes, such as SS.

In the present study, the CG of volatiles derived from SS pyrolysis was investigated over Ni/LYLC in a two-stage fixed-bed quartz reactor (TSFBQR). The effects of temperature, catalyst, and steam on the gas yield and carbon conversion were investigated. In particular, the nitrogen transformation during CG was studied to determine its possibility as a potential catalyst for clean gas production.

2. Materials and Methods

2.1. Materials

A dehydrated sludge was collected from central sewage treatment center in Gunma, Japan (Gunma sludge sample, GSS). It was pulverized to pass through a 60-mesh sieve (<250 μm) followed by desiccation at 107 °C for 24 h and then stored in an airtight container before use. Ultimate analysis was conducted with a Leco CHN-2000 elemental determinator and a Leco SC-432 sulfur determinator. The chemical components of GSS ash were determined with a Shimadzu EDX-700 energy dispersive X-ray spectrometer. Table 1 summarizes the main characteristics of the GSS. Thermal behavior of GSS was carried out in a Ulvac-Riko TGD 7000 thermogravimetric analyzer as reported previously [15].

2.2. Catalyst preparation and characterization

The catalyst was prepared by impregnation of a Loy Yang lignite (LYL; Victoria, Australia; 0.5-1.0 mm) with ammonia and aqueous solution (pH=11) of hexamine nickel (II) carbonate using a previously reported method [14]. The nickel loaded on LYL (Ni/LYL) was devolatilized at

650 °C for 1.5 h under inert atmosphere to produce Ni/LYLC.

To determine the nickel content, metals were extracted by treatment with 10% HNO₃ for 1 h. Then the solution was analyzed with a Shimadzu AA-6400F atomic absorption spectroscopy. The nickel content was detected to be 9.5 and 19.0 wt.% based on LYL and LYLC, respectively. A catalyst with a low nickel content of 2.4 wt.% (Ni/LYLC2.4) in char basis was also prepared for reference. A JEOL JEM-2010 transmission electron microscope (TEM) was employed to investigate the nickel species distribution on support material. A Mac Science M03XHF²² X-ray diffraction (XRD) and BEL BELSORP-max constant volume adsorption apparatus were used for the catalyst characterization.

A commercial Ni/Al₂O₃ catalyst (No. C13-4, Süd-Chemie Catalysts Japan, Inc., Ni loading 20 ± 2 wt.%, 0.5–1.0 mm) was employed for the CG. Sand with the same particle size was selected for non-catalytic experiment.

2.3. Gasification

CG was performed in a TSFBQR as reported previously [11]. The reactor tube (20 mm i.d. and 900 mm long) has two stages and is heated by two electrical furnaces, respectively. Argon was used as the carrier gas with a flow rate of 120 mL/min. During the experiments, temperature measurements were taken above the quartz frit, with two K-type thermocouples in the middle of the tubular reactor. For each experiment, 1 g GSS was put on the first stage and 3 g catalyst was put on the second stage. The second stage was heated up to a described temperature between 500 and 750 °C. Then the first stage was heated to 900 °C at 10 °C/min and held at that temperature for 0.5 h. The volatiles from GSS pyrolysis were streamed into the second stage for CG. If Ni/Al₂O₃ was used, the second stage was heated up to 650 °C and Ni/Al₂O₃ was reduced by H₂, followed by replacing H₂ with Ar completely. In steam CG, steam was fed through a branch inlet, which was weltd onto the main reactor at a position of 50 mm below the pyrolysis bed. When the first stage temperature reached to 100 °C, steam was generated and flowed into the reactor for the GSS volatile gasification at the second stage. The steam partial pressure in second stage and the total flow rate of the feed gas

were controlled at 30 kPa and 120 mL/min, respectively. The gaseous products (GPs) passed through two tar traps filled with deionized water (DIW) cooled in an ice-water bath for water-soluble oil (WSO) collection, while the noncondensable gases were collected in a gas bag for GC analysis. For non-catalytic test, sand was put on the second stage to the same bed height of the catalytic experiment. Soot deposited on the catalysts and reactor wall was burned out at 600 °C under an O₂ flow rate of 80 mL/min for 1 h and collected in another gas bag. When Ni/LYLC was used, the catalyst was moved out and only the soot deposited on the reactor wall was determined.

2.4. Characterization

Total carbon and nitrogen contents in the char recovered were determined with a Leco-2000 elemental determinator. H₂ and N₂ in GPs were analyzed with a Shimadzu GC/14B GC/TCD, while the carbonaceous gases were analyzed with a Shimadzu GC/14B GC/FID equipped with a methane converter to convert carbon oxides into detectable CH₄. C_nH_m represents summation of generated gaseous hydrocarbons, including ethylene, ethane, acetylene, propylene, and propane. Total organic carbon (TOC) content in WSO was determined with a Shimadzu TOC-V_{CPH} TOC analyzer. A part of CO₂ in the GPs dissolved in DIW was also determined as inorganic carbon with a TOC analyzer. NH₃ and HCN absorbed in DIW were quantified with a TOA DKK ICA-2000 ion chromatograph as reported previously [15].

3. Results and discussion

3.1. Characterization of GSS and Ni/LYLC

Prior to the CG experiments, the characteristics of the sludge sample and catalyst were first studied in this work. As listed in Table 1, GSS has low ash but high volatile yields, indicating the attractive potential for exploitation through gasification. In general, a fuel with higher volatile yield is more reactive, and therefore can be converted more easily into gas. GSS contains a high nitrogen content (5.7%), which should be taken into account because of the conversion to NO_x precursors during the pyrolysis and gasification process. The high H/C atomic ratio in GSS shows a strong aliphatic character, indicating the potential cracking performance of the GSS. The ash primarily

consists of calcium, silica, and phosphorus oxides along with small amounts of alumina, iron, and potassium oxides.

Thermogravimetry (TG) analysis provides a prior knowledge of initial and final temperatures for thermal degradation of GSS. As shown in Fig. 1, the thermal decomposition of GSS gave three main peaks in the temperature range of 150–550 °C. The first one ranging from 150 to 280 °C with a weight loss of 19.3 wt.% corresponds to the vaporization of absorbed water and the decomposition of hemi-cellulose [16]. The strong peak appearing between 280 and 390 °C reached a maximum weight loss of 40.4 wt.%, which could be caused by cellulose and lipid decomposition, while the third peak around 450 °C may be due to protein and lignin decomposition [15,17]. A slight weight loss was also observed at temperatures above 550 °C, suggesting that complete decomposition occurred. Based on the above results, 900 °C was chosen as the final pyrolysis temperature for completely releasing GSS volatiles.

Previous investigations [18,19] showed that the fine nickel particles dispersed quite well in Ni/LYLC. As shown in Fig. 2, metallic nickel, rather than nickel oxide, can be confirmed in Ni/LYLC by XRD analysis. The intensity of nickel peaks in Ni/LYLC is stronger than that in Ni/LYLC2.4, which is consistent with the high nickel content in Ni/LYLC. The average crystallite size of the nickel particles was obtained by Scherrer formula from the peak around 44°. The nickel crystallite size of Ni/LYLC was estimated to be 6.9 nm. The nickel particle size (NPS) distribution and average size was also evaluated from the TEM image (Fig. 2). The NPS distribution shows a narrow pattern and the average size is well consistent with the XRD analysis. The specific surface area and the total pore volume of the Ni/LYLC are 388 m²/g and 0.12 cm³/g, respectively. The results show that Ni/LYLC has good textural characteristic and is expected to be active for CG of GSS volatiles.

3.2. Effect of catalyst

As shown in Fig. 3, the gas yield is quite low when sand was used. About 25.9% of carbon in GSS (C_{GSS}) was converted to carbon in gas (C_{gas}), whereas 5.9% of carbon was found in WSO

(C_{wso}). The carbon loss calculated by difference is 28.0%, which should be in water-insoluble fraction (WISF) or deposited in the reactor. Quantitative determine of such lost carbon is difficult. It was reported that the WISF of biomass tar mainly consisted of pyrolytic lignin material and polycyclic aromatics. Cracking such species is difficult [20]. In this case, the GP was mainly composed of H₂, CO₂, CO, CH₄, and a substantial amount of C_nH_m. Consequently, thermal decomposition of GSS volatiles at 650 °C is not effective enough for decomposing GSS tar to GPs.

Adding Ni/LYLC2.4 to the second stage resulted in an increase in all the gas yields, except for C_nH_m. In particular, the H₂ yield is four times higher than that of non-catalytic experiment. However, the conversion to C_{gas} is yet quite low over Ni/LYLC2.4. About 30.1% of C_{GSS}, most of which should be in water-insoluble tar or deposited in the reactor, cannot be cracked to GPs over this catalyst at 650 °C. When Ni/LYLC was used at 650 °C, the gas yield increased significantly to 60.2 mmol/g (daf), while almost no C_{wso} can be detected. In this case, the GPs was mainly composed of H₂ (59.8 vol.%) and CO (32.2 vol.%). In addition, combustible gases account for 97.0 vol.% of the GPs, result in a quite high lower caloric value (LCV) of 12.3 MJ/m³ as calculated according to previous literature [21]. The H₂/CO ratio gets an expected value of 1.9 at 650 °C, which indicates the potential of the gases produced from CR of GSS volatiles over Ni/LYLC as syngas for FT synthesis. It should be noted that the CO₂ yield is lower than that from non-catalytic experiment. This could be due to CO₂ from GSS pyrolysis and subsequent volatile cracking also acts as a gasification agent that reacts with hydrocarbon gases and GSS tar. Li et al. [18] reported the same pattern in manure gasification over Ni/LYLC. At the same time, the C_nH_m disappeared during the tar cracking.

Commercial Ni/Al₂O₃ was reported to be quite active for removing coal- and biomass-derived tar [7,10]. In this study, Ni/Al₂O₃ also showed a high activity for GSS tar removal, as demonstrated in Figs. 3 and 4. The gas yield over Ni/Al₂O₃ is lower than that over Ni/LYLC, indicating that the prepared Ni/LYLC is more active than Ni/Al₂O₃ for CG of GSS volatiles. The relatively high activity of Ni/LYLC might be due to the catalysis of the supporter, i.e., LYLC, which has been

reported to possess preferable textural characteristics, such as surface area and pore volume, than commercial Ni/Al₂O₃ catalyst, and showed some improvement on the formation of light gases from manure gasification [18]. Mun et al. [8] also found that activated carbon led to a strong reduction of tar in air gasification of SS.

Besides, the yield of carbon deposited on the Ni/Al₂O₃ and reactor wall (C_{deposit}) is quite high (16.2%). Carbon deposition on the catalyst surface was reported to cover the active sites, reduce the surface area, and lead to catalyst deactivation significantly [19]. The carbon deposition on catalyst can be gasified at high temperatures by flowing steam [11]. As can be deduced from Fig. 4, almost all the carbon in volatiles was converted to C_{gas} in the presence of steam. Catalytic steam gasification over Ni/Al₂O₃ effectively promoted the production of GPs, especially H₂, as shown in Fig. 3. However, water-gas shift reactions reduced CO and CH₄ contents and promoted the formation of CO₂ and H₂ greatly. The LCV decreased from 11.9 MJ/m³ in the absence of steam to 9.7 MJ/m³ in the presence of steam over Ni/Al₂O₃ at 650 °C. Some carbon might also deposit on Ni/LYLC, but determining such carbon species is difficult due to the carbon supporter of the Ni/LYLC.

3.3. Effect of temperature

The effect of temperature on CG of GSS volatiles was investigated over Ni/LYLC. At 500 °C, Ni/LYLC showed a certain catalytic activity for decomposing GSS tar. The gas yields are quite higher in comparison with non-catalytic gasification. At the same time, the C_{wso} yield decreased to a low value of 2.5%. The gas yield increased from 31.6 mmol/g to the maximum value of 60.2 mmol/g by raising temperature from 500 to 650 °C, and then sharply decreased to 41.5 mmol/g by further raising the temperature to 750 °C. H₂ is the main GP under all the conditions. It accounts for 56.3 to 59.8 vol.% of the GPs at different temperatures. H₂/CO ratio changed from 3.2 to 1.9 when raising temperature from 500 to 650 °C, respectively. In addition, the variation trend of CO₂ is opposite with those of H₂ and CO. The decrease in CO₂ yield with raising temperature from 500 to 650 °C should be due to the enhancement of the reaction of CO₂ with hydrocarbon gases and GSS

tar, as mentioned above. The decrease in the yields of H₂ and CO and the increase of CO₂ yield at 750 °C should be due to the decline of the activity of Ni/LYLC.

It is widely known that the crystallite size of nickel particles has a decisive influence on the activity of the nickel-based catalyst [13]. The TEM images (Fig. 5) also show that the NPS of Ni/LYLC increase with raising the carbonization temperature. Sharma et al. [22] prepared carbon-based nickel catalysts from ion exchange resin and carbonized the catalyst at 500-800 °C. The XRD patterns and TEM images of the catalysts showed that the NPS become bigger as the carbonization temperature was raised. Similar result was reported by Suzuki et al. [23], who prepared crystallized and mesoporous carbon by nickel-catalyzed carbonization of wood at 700 to 900 °C. In general, a higher nickel particle crystallite size leads to a lower active surface-to-volume ratio and the decline in the activity of the nickel-based catalyst. In this study, the decreases in activity of Ni/LYLC above 750 °C should be due to the increase of the NPS. Therefore, 650 °C is suggested as the optimum temperature for the CG of GSS volatiles over Ni/LYLC.

3.4. Nitrogen distribution

As can be deduced from Fig. 6, the distribution of NCSs, especially NH₃, HCN, and N_{tar} (calculated by difference), strongly depended on temperature and catalyst. When sand was used, the nitrogen in volatiles (N_{volatile}) released was mainly converted to NH₃ and N_{tar}. Only 16.8% of the NCSs is in the form of N₂, indicating that thermal decomposition of N_{volatile} at 650 °C is not effective for decomposing the NO_x precursor, i.e., NH₃, HCN, and N_{tar}, to N₂. High-temperature gasification of SS above 850 °C also release large amount of NH₃, HCN, and N_{tar} [12]. Therefore, it is necessary to find a way to reduce the release of the NO_x precursor. An alternative strategy is the simultaneous decomposition of the NO_x precursor during CG.

As Fig. 6 illustrates, the N_{tar} yield over Ni/LYLC2.4 decreased greatly in comparison with non-catalytic experiment. N_{tar} was mainly decomposed to N₂ and NH₃ over Ni/LYLC2.4. The nitrogen distribution changes dramatically when Ni/LYLC was used. The CG of N_{volatile} over Ni/LYLC mainly afforded N₂. Negligible amounts of NH₃ and HCN were detected in this case.

Ni/Al₂O₃ shows perfect activity for removing NO_x precursor in comparison with Ni/LYLC. It should be noted that almost all the NH₃, HCN, and N_{tar} were converted to N₂. The high activity of Ni/Al₂O₃ for N_{volatile} conversion to N₂ is in accordance with its high nickel content. Mojtahedi and Abbasian [24] studied the activity of Ni/Al₂O₃ catalysts with different nickel loadings and found that NH₃ conversion strongly depended on the nickel content in the catalyst, and the largest NH₃ conversion was obtained over a catalyst with the highest nickel content.

The effect of temperature on the nitrogen distributions over Ni/LYLC was investigated at 500-750 °C. As displayed in Fig. 6, almost no HCN can be detected at 500 °C, indicating that Ni/LYLC is active enough for HCN decomposition at the temperature. The high activity of Ni/LYLC for HCN decomposition at 500 °C agrees well with the study by Osińska [25], who demonstrated the catalytic behavior of nickel catalyst for the destruction of HCN. The decomposition of N_{tar} and HCN at 500 °C mainly afforded NH₃ and N₂ in the yields higher than those from non-catalytic test. However, the activity of Ni/LYLC for NH₃ decomposition is still quite low at 500 °C. Wang et al. [26] also demonstrated the low activity of Ni-based catalyst for NH₃ decomposition at 500 °C. The conversion to N₂ increased from 28.0 to 67.3% by raising temperature from 500 to 650 °C and then sharply decreased to 36.5% when further raising the temperature to 750 °C. This trend is well consistent with the activity for GSS tar decomposition. The increase in the crystallite size of the nickel particles at 750 °C leads to the deactivation of Ni/LYLC for NO_x precursor decomposition. Thus, 650 °C is the optimum temperature for converting GSS N_{volatile} to N₂.

4. Conclusions

The present study demonstrates that the prepared Ni/LYLC is quite active not only for the CG of GSS volatiles to H₂-rich syngas, but also for conversion of N_{volatile} to N₂ at 650 °C. Simultaneous catalysis of its char supporter makes Ni/LYLC more active than the commercial Ni/Al₂O₃. The CG of GSS volatiles significantly depended on the temperature and catalyst, and the CG over Ni/LYLC above 650 °C resulted in the increase of NPS and the deactivation of Ni/LYLC for volatiles

gasification. Decreasing the carbon deposition and assessment of its lifetime may significantly improve the industrial feasibility of the **Ni/LYLC**.

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Figure captions

Table 1 Characteristics of GSS.

Fig. 1. TG and DTG curve of GSS.

Fig. 2. XRD patterns (a) and TEM images (b) of Ni/LYLC and Ni/LYLC2.4.

Fig. 3. Effects of temperature, catalyst, and steam on gas yields.

Fig. 4. Effects of temperature, catalyst, and steam on carbon distributions.

Fig. 5. TEM images of Ni/LYLC carbonized at different temperatures for 0.5 h.

Fig. 6. Effects of temperature and catalyst on nitrogen distributions.

Table 1

Characteristics of GSS.

Proximate analysis (wt.%) ^a				Ultimate analysis (wt.%, daf)				<i>S</i> _{t,d} (wt.%)	H/C
<i>M</i> _{ar}	<i>A</i> _d	<i>V</i> _d	<i>FC</i> _d ^b	C	H	N	O ^b		
73.6	11.7	78.1	10.2	50.5	7.2	5.7	>35.9	0.7	1.6990
Ash analysis (expressed as wt.% of metal oxides)									
CaO	P ₂ O ₅	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	CuO	ZnO	others
31.0	20.2	22.0	12.5	7.8	3.0	2.2	0.4	0.7	0.2

^aM: moisture; A: ash; V: volatile content; FC: fixed carbon; ar: as received basis; d: dried basis; daf: dried and ash-free basis; *S*_{t,d}: total sulfur in dried basis.

^bCalculated by difference.

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