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Low-temperature catalytic gasification of sewage sludge-derived volatiles to produce clean H_2-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 N_2. Ni/LYLC proved to be quite active not only for tar reduction, but also for the conversion of VNSs to N_2 at 650 °C. CG of SSDVs over Ni/LYLC produced significant amount of clean H_2-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 H_2-rich syngas.

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 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 H_2-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

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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 NH_3, HCN, and nitrogen in tar (N_{tar}) during pyrolysis and then converted to NO_x and N_2O 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 H_2 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 NH_3 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 yields and carbon conversions were investigated. In particular, the nitrogen transformation during CG was studied to determine its possibility as a potential catalyst for clean gas production.

Materials and methods

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].

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 hexammine 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% HNO_3 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 M03XHF[22] X-ray diffraction (XRD) and BEL BELSORP-max constant volume adsorption apparatus were used for the catalyst characterization.

A commercial Ni/Al_2O_3 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.

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

Table 1 – Characteristics of GSS.

Proximate analysis (wt.%)[a]				Ultimate analysis (wt.%, daf)				$S_{t,d}$ (wt.%)	H/C
M_{ar}	A_d	V_d	FC_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_2O_5	SiO_2	Al_2O_3	Fe_2O_3	K_2O	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

[a] M: 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.
[b] Calculated by difference.