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Nitrogen transformation during gasification of livestock compost over transition metal and Ca-based catalysts

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HIGHLIGHTS

- Nitrogen transformation during catalytic gasification of pig compost was investigated.
- Thermal decomposition below 750 °C is not effective for removal of volatile nitrogen.
- Transition metal catalysts are active for converting the volatile nitrogen to N_2.
- Ca-based catalysts significantly promote the conversion of volatile nitrogen to NH_3.

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ABSTRACT

Catalytic gasification of a pig compost (PC) was investigated over transition metal catalysts (TMCs, including limonite, $CoMo/Al_2O_3$, Ni/Al_2O_3, and nickel loaded on lignite char) and Ca-based catalysts (dolomite and CaO) in a two-stage fixed-bed reactor to understand the effects of catalyst, temperature, and steam on nitrogen distributions. Non-catalytic thermal decomposition (TD) of PC volatiles below 750 °C is not effective for decomposing the entire volatile nitrogen species (VNSs) to N_2. NH_3 was found to be the predominant nitrogenous gas under inert conditions used in this investigation, and its yield increased with raising TD temperature. The N yield in HCN is lower than 5% below 550 °C, and sharply increased to 13.9% at 750 °C due to TD of volatiles. Most of VNSs were converted to N_2 over TMCs, especially over Ni-based ones. The TMCs proved to be quite active not only for tar reduction, but also for VNSs decomposition at 450–650 °C. On the contrary, CaO-based catalysts, especially dolomite, significantly promoted the conversion of VNSs to NH_3. Ni/Al_2O_3 effectively promoted the conversion of NH_3 and HCN to N_2 at 550 °C. Steam introduced mainly prevented HCN decomposition over dolomite and coke deposition over Ni/Al_2O_3. This study provides a basic insight into the nitrogen transformations during catalytic gasification of PC, which would benefit the clean utilization of PC as an energy source.

1. Introduction

The disposal of livestock manure (LSM) becomes a growing problem due to its high potential for pollution and increasing production. In general, LSM is a potential source of pathogen-containing wastes, which emits ammonia, greenhouse gases, and odorous compounds, causing water contamination and air pollution. The traditional disposal routes of LSM, including agricultural application and landfill, are facing more and more pressure due to land limitations and stringent regulations [1,2]. Thus, it is important to develop a cost-effective and ecofriendly solution to replace those traditional disposal technologies.

Alternatively, using LSM as a biomass for energy production via biological and thermochemical conversion technologies is regarded as an environmentally acceptable disposal route with potential financial benefits. Anaerobic digestion is one of biological means for decomposing LSM in an oxygen-free environment, and has the advantage of producing biogas [3]. Several thermochemical conversion technologies, including pyrolysis, gasification, combustion, and liquefaction, are currently under development [3,4]. Among these processes, gasification is an efficient method for converting biomass wastes to energy or syngas [4,5]. Catalytic gasification (CG) of LSM successfully produced the hydrogen-rich gas over

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Nomenclature

CBCs	Ca-based catalysts
C_{char}	carbon in char
$C_{deposit}$	carbon deposited on the catalyst and reactor wall
CG	catalytic gasification
C_{gas}	carbon in gas
CR	catalytic reforming
C_{WSO}	carbon in WSO
DIW	deionized water
GPs	gaseous products
HCV	high calorific value
LSM	livestock manure
NBCs	Ni-based catalysts
N_{char}	in char
NCSs	nitrogen-containing species
N_{PC}	nitrogen in PC
NPSs	Ni particle sizes
N_{tar}	nitrogen in tar
$N_{volatile}$	nitrogen in volatiles
N_{WSO}	nitrogen in WSO
PC	pig compost
RT	room temperature
TD	thermal decomposition
TMCs	transition metal catalysts
TN	total nitrogen
TOC	total organic carbon
TSFBQR	two-stage fixed-bed quartz reactor
WISP	water-insoluble portion
WSO	water-soluble oil
XRD	X-ray diffraction

Ni-based catalysts (NBCs) [6–10]. However, LSM usually contains large amounts of organonitrogen species, which are converted to NO_x precursors such as NH_3, HCN, and nitrogen in tar (N_{tar}) during pyrolysis and then to NO_x and N_2O during gasification and combustion, causing significant environmental pollution [11,12]. It is of great significance to understand the release behaviors of nitrogen-containing species (NCSs) and their transformation during pyrolysis and decomposition of LSM volatiles. There is much information available on the formation and decomposition of NCSs during pyrolysis and gasification of coals and biomass, but little information on LSM is available.

Many catalysts, such as dolomite, CaO, olivine, alkali metals, transition metals, and activated carbon-supported catalysts, have been used for biomass gasification [13,14]. Among them, the transition metal catalysts (TMCs), especially nickel-, iron- and cobalt-based ones, are active for biomass tar decomposition to produce hydrogen-rich gas and syngas [6–9,13,14]. Limonite is a naturally occurring iron ore with a high iron content and was used for tar decomposition [13]. Dolomite is widely used as the secondary catalyst to minimize tar content in biomass gasification, and the presence of CaO in dolomite might be responsible for its activity for tar conversion [13].

In the present study, we focus on CG of a pig compost (PC) over TMCs and Ca-based catalysts (CBCs) in a two-stage fixed-bed quartz reactor (TSFBQR). The effects of catalyst, temperature, and steam on the nitrogen distributions were investigated. Prior to the CG experiments, nitrogen distribution during thermal decomposition (TD) was first studied in this work.

2. Experimental

2.1. Materials

The PC was obtained from a piggery in the Gunma Prefecture, Japan. It was pulverized to pass through a 16-mesh sieve (<1.18 mm) followed by oven-dried at 107 °C for 24 h and then storage in an airtight container before use. Ultimate analysis was conducted with a Leco CHN-2000 elemental determinator and a Leco SC-432 sulfur determinator. High calorific value (HCV) was determined with a Shimadzu CA-4PJ auto-calculating bomb calorimeter. Table 1 summarizes the main characteristics of the PC sample.

Four TMCs, including commercial Ni/Al_2O_3 (No. C13-4, Süd-Chemie Catalysts Japan, Inc., Ni loading 20 ± 2 wt.%, 0.5–1.0 mm) and $CoMo/Al_2O_3$ (SC20-6, CoO: 3.0–4.0 wt.%, MoO_3: 13.0–15.0 wt.%), a limonite ore (Indonesian), and nickel loaded on Loy Yong lignite char (Ni/LYLC, Ni loading 9 ± 1 wt.%) [15], and two CBCs (i.e., CaO and calcined dolomite) were used for the CG. The CBCs were calcined at 1200 °C for 1 h before use. The main component in calcined limonite and dolomite was determined by a Shimadzu EDX-700 energy dispersive X-ray spectrometer and the results are shown in Table 2. A Mac Science M03XHF^{22} X-ray diffraction (XRD) and BEL BELSORP-max constant volume adsorption apparatus were used for the catalyst characterization. The Ni loadings and Ni particle sizes (NPSs) in the Ni/Al_2O_3 and Ni/LYLC were determined as reported previously [16]. The main characteristics of the catalysts are shown in Table 3.

Table 1
Characteristics of the PC sample.

Proximate analysis (wt.%)[a]			Ultimate analysis (wt.%, daf)				$S_{t,d}$ (wt.%)	HCV (MJ/kg)
M_{ar}	A_d	VM_{daf}	C	H	N	O[b]		
27.6	19.2	81.8	49.3	6.8	5.1	>38.1	0.7	15.9

[a] M_{ar}: moisture (received basis); A_d: ash (dried basis); FC_{daf}: fixed carbon (dried and ash-free basis); VM_{daf}: volatile matter (dried and ash-free basis); d: dried basis; daf: dried and ash-free basis; $S_{t,d}$: total sulfur in dried basis.
[b] Calculated by difference.

Table 2
Chemical composition (wt.%) of the limonite and calcined dolomite.

Sample	Fe_2O_3	SiO_2	Al_2O_3	NiO	Co_2O_3	Cr_2O_3	CaO	MgO
Limonite	65.00	1.67	11.24	1.69	0.13	1.70	0.07	0.25
Calcined dolomite	0.12	0.38	0.23				96.70	0.32