Catalytic reforming of volatiles and nitrogen compounds from sewage sludge pyrolysis to clean hydrogen and synthetic gas over a nickel catalyst

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Abstract

Low-temperature catalytic reforming of volatiles and nitrogen compounds from sewage sludge (SS) pyrolysis was performed in a two-stage fixed-bed reactor over Ni/Al₂O₃ under inert and steam-reforming conditions. The results show that the reforming of SS volatiles significantly depended on catalyst temperature, space velocity, steam partial pressure, and feedstock type. Catalytic cracking of SS volatiles at 650 °C under inert atmosphere produced a tar-free synthetic gas with a H₂/CO ratio of 2:1 in a high yield, which is preferred for maximum conversion efficiency for methanol synthesis. Steam as the gasifying agent gave a H₂-rich gas (H₂ content 68.0 vol.%) with a high yield of 82.5 mmol/g-daf at 650 °C, while the H₂ yield is twice as that from non-steam gasification. Ni/Al₂O₃ effectively improved tar reforming and showed great resistance to coke deposition in the presence of steam. NH₃, HCN, and tar-N are the main volatile nitrogen species in SS pyrolysis. Almost all the NO_x precursors were converted to N₂ when catalytic reforming at 650 °C both in the presence and absence of steam. Such an approach may lead to the development of a clean SS utilization technology and also H₂/synthetic gas production technology from SS.

Keywords: Sewage sludge; Catalytic gasification; Hydrogen; Low-temperature; Nitrogen transformation.

1. Introduction

Recently, thermochemical conversion of sewage sludge (SS) for energy production is regarded

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as an alternative disposal route with potential financial benefits instead of its less acceptable common disposal processes, including agricultural application, landfill, and incineration [1-4]. Gasification is considered as one of the most promising thermochemical technology that converts sludge waste into H₂-rich gas or combustible gas primarily composed of CO, H₂, and CH₄, which can be used as a fuel to generate electricity and heat or as raw material for chemical synthesis processes [5,6]. Gasification is also advanced in reducing waste volume, removing toxic organic compounds and fixing heavy metals in the resulting solid [7,8]. However, the development of sludge gasification (SG) is challenged by the production of tar and nitrogen compounds.

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 [9]. Many attempts, e.g., optimization of gasification conditions and gasifier design, thermal cracking, and catalytic cracking, have been made to remove tar from SG [6,9,10]. Among the techniques, catalytic cracking is regarded as one of the promising techniques for tar removal at moderate conditions [11]. A lot of catalysts, such as dolomite, CaO, olivine, alumina, zeolite, and activated carbon have been studied in inert, steam, air, and air-steam gasification of SS [9,11-14]. These catalysts are active for SS tar decomposition to produce H₂-rich and synthetic gas at temperature higher than 800 °C. Since the high ash content in SS causes the slagging and fouling in thermal conversion systems when a gasifier is operated at high temperature [15], it is essential to develop low-temperature SG technology.

In general, SS contains large amount of nitrogen, which may result in a significant emission of NO_x precursors, such as NH₃, HCN, and nitrogen in tar (tar-N) during SS pyrolysis and gasification [16,17]. Understanding the releasing behaviors of nitrogen-containing species (NCSs) during pyrolysis and gasification and reducing the emission of NO_x precursors are important for clean H₂ and synthetic gas production. Many researchers investigated the formation and distribution of NCSs from pyrolysis and gasification of coal and biomass [18], but few reports were issued on the catalytic decomposition of NCSs during SS gasification, especially for low-temperature

52 gasification.

53 Nickel-based catalysts proved to be quite active not only for tar reduction, but also for NH₃
54 decomposition [18]. Therefore, the present study focuses on simultaneous tar and NCS
55 decomposition during low-temperature **catalytic reforming (CR) and catalytic steam reforming**
56 **(CSR)** of SS **volatiles** for H₂ and synthetic gas production using a two-stage fixed-bed reactor. A
57 commercial Ni/Al₂O₃ was employed to study the effects of the most important operational
58 parameters in gasification, i.e., temperature, atmosphere, space velocity (SV), **steam** partial pressure
59 **(SPP)**, and feedstock **type**, on the gas yields and carbon balances. Especially, the nitrogen
60 transformation during **CR of SS volatiles** was studied to determine its possibility as a potential
61 catalyst for clean gas production. Prior to the **CR** experiments, the thermal characteristics of the **SS**
62 samples **were** first investigated.

63 **2. Experimental**

64 *2.1. Materials*

65 A dehydrated sludge collected from central sewerage treatment centre in Gunma, Japan (GSS)
66 and a dried SS obtained from Nippon Steel Co., Japan (NSS) were used in this study. The samples
67 were pulverized to pass through a 60-mesh sieve (<250 μm) followed by **desiccation** at 107 °C for
68 24 h and then stored in an airtight container before use. Ultimate analysis was conducted with a
69 Leco CHN-2000 elemental determinator and a Leco SC-432 sulfur determinator and proximate
70 analysis was carried out in a Leco TGA701 proximate analyzer. Table 1 shows the proximate and
71 ultimate analyses of the **SS** samples. The chemical compositions of **SS** ashes determined with a
72 Shimadzu EDX-700 energy dispersive X-ray spectrometer are summarized in Table 2.

73 A commercial Ni/Al₂O₃ (No. C13-4, Süd-Chemie Catalysts Japan, Inc., Ni loading 20 ± 2 wt%,
74 0.5–1.0 mm) was employed for SG. Sand with the same particle size was selected for non-catalytic
75 experiment.

76 *2.2. Thermogravimetric analysis*

77 Thermal behavior of the GSS was carried out in a thermogravimetric analyzer (TGD 7000,

78 ULVAC-RIKO, Japan). About 50 mg of GSS was placed in a pottery crucible and heated at $10\text{ }^{\circ}\text{C} \cdot$
79 min^{-1} from ambient temperature to $900\text{ }^{\circ}\text{C}$ under a dry argon flow of $80\text{ mL} \cdot \text{min}^{-1}$. The
80 thermogravimetry (TG) and derivative thermogravimetry (DTG) data were obtained using the
81 software in the analyzer. The gaseous product was collected from 150 to $900\text{ }^{\circ}\text{C}$ in an interval of
82 $150\text{ }^{\circ}\text{C}$ for gas chromatography (GC) analysis.

83 2.3. Gasification

84 As shown in Fig. 1, SG was performed in a two-stage fixed-bed quartz reactor as reported
85 previously [19]. The reactor tube (20 mm i.d. and 900 mm long) has two stages and is heated by
86 two electrical furnaces. Argon was used as the carrier gas with a flow rate of $120\text{ mL} \cdot \text{min}^{-1}$ and the
87 SV in the catalyst was 4000 h^{-1} . During the experiment, the SS sample and the $\text{Ni}/\text{Al}_2\text{O}_3$ were put
88 on the first and second stages, respectively, for of the volatile reforming. The second stage was
89 heated up to $650\text{ }^{\circ}\text{C}$ and $\text{Ni}/\text{Al}_2\text{O}_3$ was reduced by H_2 for 1 h. After H_2 was replaced by Ar
90 completely, the second stage was kept at a described temperature between 400 to $750\text{ }^{\circ}\text{C}$. Then the
91 first stage was heated to $900\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ and held at the temperature for
92 0.5 h. The volatiles from SS pyrolysis were streamed into the second stage for decomposition. For
93 steam SG, steam was fed through a branch inlet, which was weltd onto the main reactor at a
94 position of 50 mm below the biomass pyrolysis bed. When the first stage temperature reached to
95 $100\text{ }^{\circ}\text{C}$, steam was generated and flowed into the reactor for the SS volatile gasification at second
96 stage. The SPP in the second stage was controlled at 30, 45, and 60 kPa and the total flow rate of the
97 feed gas was kept at $120\text{ mL} \cdot \text{min}^{-1}$. The gaseous products passed through two tar traps with
98 deionized water (DIW) cooled in an ice-water bath while the noncondensable gases were collected
99 in a gas bag for GC analysis. Soot deposited on the catalyst and reactor wall was burned out at
100 $600\text{ }^{\circ}\text{C}$ under an O_2 flow rate of $80\text{ mL} \cdot \text{min}^{-1}$ for 1 h and collected in another gas bag.

101 2.3. Characterization

102 Total carbon and nitrogen contents in char recovered were determined with a Leco-2000
103 elemental determinator. H_2 and N_2 in gas phase were analyzed with a Shimadzu GC-14B GC/TCD,

104 while the carbonaceous gases were analyzed with a Shimadzu GC-14B GC/FID equipped with a
105 methane converter to convert carbon oxides into detectable CH₄. C_nH_m represents summation of
106 generated gaseous hydrocarbons, including ethylene, ethane, acetylene, propylene, and propane.
107 Total organic carbon (TOC) content in the tar traps was determined with a Shimadzu TOC-V_{CPH}
108 TOC analyzer. NH₃ and HCN absorbed in DIW were quantified with a TOA-DKK ICA-2000 ion
109 chromatography as reported [20].

110 3. Results and discussion

111 3.1. Characterization of the SS samples

112 As listed in Table 1, volatile contents in both SS samples are higher than 82.1% (wt%, daf),
113 indicating the possibility for using as biomass resources. The ash content in NSS is higher than that
114 in GSS. However, as shown in Table 2, the ash either in NSS or in GSS mainly consists of CaO,
115 P₂O₅, and SiO₂. In addition, nitrogen and sulfur contents in NSS are much higher than those in GSS,
116 which should be taken into account because of the conversion to NO_x and SO_x precursors during the
117 pyrolysis and gasification process. The high H/C atomic ratio in SS samples shows their low
118 aromatic character, indicating the potential cracking performance of the SS samples.

119 As shown in Fig. 2, the thermal decomposition of GSS mainly occurred at 150-550 °C. GSS
120 pyrolysis at 150-300 °C caused a weight loss of 22.5%, which corresponds to the hemicellulose
121 decomposition [21]. However, the gas yield is quite low in the temperature range, suggesting that
122 GSS volatiles released are mainly present in tar. Raising temperature from 300 to 450 °C leads to
123 the highest peak in DTG curve with a weight loss of 41.7%. At the same time, the gas yields reach
124 the highest value of 7.7 mmol/g-daf, with a gas composition of CH₄, C_nH_m, CO, and CO₂. SS
125 pyrolysis mainly occurred in this temperature range and gave the maximum evolution amount of
126 gaseous products [22,23]. When the temperature was raised from 450 to 600 °C, 5.7% of volatiles
127 was released from GSS and gave a gas yield of 2.9 mmol/g-daf. Main components in the gas are
128 CH₄, C_nH_m, and CO₂. The significant release of carbonaceous gas at 300-600 °C is well consistent
129 with the results reported that the CH₄ and CO were mainly produced from the cracking of methoxyl

130 and carbonyl groups, respectively, during pyrolysis of biomass model compounds, i.e., cellulose,
131 hemicellulose, and lignin [24]. Further raising the temperature from 600 to 900 °C, a negligible
132 weight loss was found, indicating that volatile release was nearly complete at 600 °C. H₂ is the main
133 gaseous product in this temperature range, similar to lignin pyrolysis [24]. It should be noticed that
134 GSS pyrolysis above 750 °C gave a high yield of CO. Lignin pyrolysis was reported to start at 600
135 °C and give a maximum release of CO at 800 °C [24]. In this work, CO released above 750 °C
136 should be due to the pyrolysis of lignin in GSS. Based on the above results, 900 °C was chosen as
137 the final pyrolysis temperature for completely releasing the SS volatiles.

138 3.2. Effect of temperature on CR

139 CR of the GSS volatiles was conducted at 400-750 °C. The same amount of sand was used for
140 non-catalytic experiment at 650 °C. As shown in Fig. 3a, the gas yield is quite low when sand was
141 used. About 25.9% of carbon in GSS (GSS-C) was converted to carbon in gas (gas-C), whereas
142 5.9% of carbon was found in water-soluble oil (WSO-C). In this case, the carbon balance is poor.
143 The carbon loss calculated by difference is 28.0%, which should be in water-insoluble fraction or
144 deposited in the reactor and difficult to be detected. Even at 400 °C, Ni/Al₂O₃ showed a certain
145 catalytic activity for decomposing GSS tar. The carbon balance increased to 94.9%, and almost no
146 WSO-C was detected. GSS tar was mainly decomposed to H₂, CO₂, and CH₄ at 400 °C. The gas
147 yields are quite higher in comparison with non-catalytic gasification. However, the conversion to
148 gas-C is yet quite low at 400 °C, and most of the carbon from tar cracking should be converted to
149 deposit-C (carbon deposited on the Ni/Al₂O₃ surface and reactor wall).

151 When raising the temperature from 400 to 750 °C, the gas yield increased significantly and
152 reached the maximum value of 59.0 mmol/g-daf, which is four times higher than that from
153 non-catalytic gasification. The yields of CH₄ and CO₂ decreased with raising temperature and
154 reached to 0.5 and 1.3 mmol/g-daf, respectively. At the same time, the yields of H₂ and CO
155 increased significantly. Ni/Al₂O₃ was reported to be very active for CR of CH₄ with CO₂ (eq. 1),

and the activity increased with raising temperature [25]. At 750 °C, the total yield of H₂ and CO account for 97.0 vol.% of the gaseous products. The lower heating value (LHV) of the gaseous products was calculated and the result shows that the LHV decreased from 16.2 to 11.4 MJ/m³ with raising the temperature from 400 to 700 °C. In general, CH₄ has highest heating value in the gaseous products. The sharply decrease of CH₄ content leads to a decrease in the LHV of the gaseous products. Moreover, the H₂/CO ratio get an expected value of 2.0 at 650 °C, indicating that the potential use of the gas produced from CR of GSS volatiles over Ni/Al₂O₃ as synthetic gas for FT synthesis. No WSO-C was detected and the carbon balance reached approximately 100% during CR of GSS volatiles above 500 °C, indicating that Ni/Al₂O₃ is active enough for GSS decomposition in this temperature range. However, the deposit-C yield is yet quite high even at 750 °C. Carbon deposition on the catalyst surface was reported to cover the active sites, reduce the surface area, and lead to catalyst deactivation significantly [26,27]. Consequently, CR of GSS volatiles over Ni/Al₂O₃ can produce a good quality tar-free synthetic gas in high yield at 650 °C. However, it is necessary to develop a strategy for avoiding the carbon deposition on the catalyst.

3.3. Effect of temperature on CSR

The carbon deposition on catalyst can be gasified at high temperatures by flowing either CO₂ or steam [26]. In the techniques, CSR is considered as an efficient method for large-scale H₂ production via the reaction of tar with steam at temperatures around 650–700 °C. During CSR, the carbon deposition is suppressed by steam, which favors the reforming reactions. Thus, CSR of GSS volatiles was investigated in a SPP of 30 kPa at 400–650 °C.

As Fig. 3 displays, no obvious difference can be found between inert and steam reforming of GSS volatiles without Ni/Al₂O₃, indicating that feeding steam leads to little improvement on the non-catalytic reforming of GSS volatiles. Different from CR at 400 °C, CSR decomposed all the

182 tarry materials and gave a higher H₂ yield, via the steam reforming reactions (eq. 2). At the same
 183 time, additional H₂ and CO₂ were produced through the water-gas shift reactions (WGSR, eqs. 3
 184 and 4). When raising the temperature from 400 to 650 °C, the gas yield increased significantly to a
 185 yield of 82.5 mmol/g-daf. The H₂ composition is 66.6 vol.% at 500 °C. This value increased to the
 186 maximum of 70.0 vol.% when raising the temperature to 550 °C. CSR of biomass and bio-oil over
 187 Ni/Al₂O₃ at 500-700 °C also gave the similar H₂ composition [28]. The H₂ yield and tar removal in
 188 this study over Ni/Al₂O₃ are higher compared to high-temperature gasification of SS using additives,
 189 such as dolomite and activated carbon [9-14]. Therefore, Ni/Al₂O₃ can be used as a potential
 190 catalyst for low-temperature steam gasification of SS for H₂ production:

192 Although the H₂ yield increased a lot from 550 to 650 °C, but the H₂ composition slightly
 193 decreased from 70.0 to 68.0%, due to the remarkably increase of CO in the gaseous products. As
 194 shown in Fig. 3b, 13.4% of deposit-C was produced at 500 °C, indicating that WGSR below 500 °C
 195 is insufficient for deposit-C gasification. The deposit-C yield decreased significantly to 6.0% at 550
 196 °C and further decreased to a negligible level when raising temperature to 650 °C. The decrease in
 197 deposited-C yield and the increase in the CO yield during CSR should result from the WGSR of
 198 eq.5. Generally, this reaction scarcely occurs below 800 °C in the absence of catalyst [29]. Tomita et
 199 al. [30] reported that the well-dispersed nickel particles significantly catalyzed steam gasification of
 200 brown coal at 600 °C. Gasification of the deposit-C below 650 °C in this study was ascribed to the
 201 presence of the nickel catalyst. The significant increase of CO yield with raising temperature to 650
 202 °C indicates that the WGSR is predominant in this temperature range. Thus, CSR of GSS volatiles
 203 over Ni/Al₂O₃ at 650 °C is favorable for avoiding carbon deposition.

204 The LHV of the gaseous products obtained from CSR at 650 °C was calculated to 9.7 MJ · m⁻³,
 205 which is lower than that from CR, partly because of the rich in CO₂. In this case, the H₂/CO ratios
 206 reached 9.8 and 4.6 at 550 and 650 °C, respectively. Therefore, CSR of GSS volatiles over Ni/Al₂O₃
 207 is favorable not only for producing tar-free H₂-rich gas, but also for avoiding carbon deposition on

208 catalyst, at 650 °C.

209 3.4. Effect of *SPP*

210 Feeding a sufficient amount of steam into the reactor is necessary for producing a high yield of
211 H₂. In steam gasification, the excess steam can be easily separated by condensation. The effect of
212 *SPP* was studied by changing the *SPP* from 30 to 53 kPa at 500 °C. As shown in Fig. 3, the total gas
213 yield and H₂ selectivity increased with increasing *SPP*. The higher of *SPP* results in higher H₂ and
214 CO₂ contents and lower CO and CH₄ concentrations due to the enhancement of *WGSR* during the
215 *CSR* process, which is well consistent with the results reported [31,32]. A high *SPP* improves *CSR*
216 and displaces *WGSR* equilibrium towards H₂ formation. When the *SPP* was increased to 53 kPa,
217 more than 83.7% of gas-C was converted to CO₂, resulting in a low LHV of 8.9 MJ · m⁻³ in
218 comparison with the value of 10.8 MJ · m⁻³ obtained at 30 kPa. At the same time, the deposit-C yield
219 decreased slightly with increasing *SPP*, due to the inhibition of carbon deposition by the enhanced
220 *WGSR*. However, higher *SPP* requires more external heat supply. Thus, it should be controlled and
221 adjusted at appropriate *SPP* to produce suitable H₂-rich gas and synthetic gas.

222 3.5. Effect of *SV*

223 The decrease of *SV*, in other word the increase of residence time, is beneficial for the catalytic
224 reactions at catalyst bed. The *SV* was increased twice as the initial value by decreasing the packed
225 catalyst volume half during *CSR* of GSS volatiles at 650 °C with a *SPP* of 30 kPa. Obviously,
226 increasing the *SV* to 8000 h⁻¹ reduces the gasification efficiency, especially for H₂ production,
227 because of the short residence time, as shown in Fig. 4a. As Fig. 4b illustrates, the high *SV* also
228 increases carbon deposition. These results well accord with those reported by Uddin et al. [33].
229 Lower *SV* and longer residence time favors higher carbon conversion and higher gas production.

230 3.5. Effect of feedstock type

231 *CSR* of NSS and GSS volatiles were carried out at 400 and 650 °C in a *SV* of 4000 h⁻¹ and a
232 *SPP* of 30 kPa. As can be deduced from Fig. 5, there has no obvious difference of total gas yield
233 between *CSR* of NSS and GSS volatiles at 400 °C. However, the CO₂ yield obtained from GSS is

higher than in NSS, which should be due to the relatively high oxygen content in GSS, as shown in Table 1. CSR of NSS volatiles get a synthetic gas with similar gas composition with GSS when CSR at 650 °C. In general, biomass with a higher volatile matter content corresponds to the higher gas yield. On the contrary, the total gas yield of NSS (82.5 mmol/g-SS) is higher than GSS (98.8 mmol/g-SS), even if GSS contains more volatiles than NSS, as lists in Table 1. It can be explained that, compared with GSS, NSS contains higher carbon and hydrogen contents, which might react with steam, results in more H₂ and CO in the gaseous products. Usually, the higher the oxygen content in biomass, the lower H₂ is produced [34]. For efficient CSR processes for H₂ production, low oxygen content feedstock is desirable.

3.6. Nitrogen distribution

As Table 1 illustrates, the SS samples contain significant amount of nitrogen, which will be converted to NO_x precursors, such as NH₃, HCN, and tar-N during pyrolysis and gasification. The nitrogen distributions from CR and CSR of GSS volatiles were studied in order to determine the environmental feasibility of the SG process.

3.6.1. CR

As Fig. 6 illustrates, the release of nitrogen in GSS shows a different pattern from that of carbon, in detail ca. 37.0% of carbon retained in char (char-C), while only ca. 23.0% of nitrogen was found in char (char-N). This trend indicates that nitrogen released more easily than carbon during SS pyrolysis. Without Ni/Al₂O₃, the nitrogen in volatiles (volatile-N) released was mainly converted to NH₃ and diff-N (calculated by difference). The diff-N should be mostly in the form of tar-N or nitrogen deposited in the catalyst. NH₃ (25.8%) is the main nitrogen-containing gaseous product and only 2.4% of nitrogen is in the form of HCN. The formation of NH₃ should be partly due to the amino structures in the SS, while the thermal cracking of volatiles is the main route of HCN formation [20,35]. Similar to the results reported [35], GSS pyrolysis at a low heating rate of 10 °C·min⁻¹ results in a relatively low HCN yield. However, only 16.8% of nitrogen was converted to N₂, indicating that secondary thermal decomposition of volatile-N at 650 °C is not effective in

decomposition of the entire NO_x precursor to N₂. High-temperature pyrolysis and gasification of SS above 800 °C also released large amount of NO_x precursors [16,17]. Thus, it is necessary to find a way to reduce the release of the NO_x precursors. An alternative strategy is simultaneous decomposition of the NO_x precursors during catalytic SG.

As shown in Fig. 6, CR of GSS volatiles at 400 °C resulted in the conversion of large amount of volatile-N to NH₃. However, the catalytic activity of Ni/Al₂O₃ at 400 °C for NH₃ decomposition is yet quite low. This trend is consistent with a Ni-based catalyst, which demonstrated negligible activity for NH₃ decomposition at 400 °C [36]. At the same time, almost no HCN can be detected even at 400 °C, suggesting that Ni/Al₂O₃ is active enough for decomposing HCN. HCN can also be converted to NH₃ by subsequent reaction with H₂ (eq. 6). The high activity of Ni/Al₂O₃ for HCN decomposition agrees well with the study by Osińska [37], who demonstrated the catalytic behavior of nickel catalyst for the destruction of HCN. The NH₃ decomposition (eq. 7) activity was markedly enhanced by raising temperature from 400 to 500 °C, at which the NH₃ yield decreased sharply from 31.7% to 3.5%, and then decreased to a negligible amount when further raising temperature to 550 °C. The increase of H₂ yield in this temperature range should partly be ascribed to the NH₃ decomposition. CR of volatile-N over Ni/Al₂O₃ mainly afforded N₂, the yield of which increased from 19.9% to 49.9% with raising temperature from 400 to 500 °C and reached to the maximum value of 74.3% at 650 °C. In addition, no obvious change of N₂ yield can be found when further raising temperature to 750 °C. The nitrogen balance reached the desired value of higher than 98% above 650 °C, indicating that CR of volatile-N was almost complete at 650 °C. The results correspond to the previous studies on NH₃ decomposition from pyrolysis of coal and biomass over supported metals [18,35,38], in which Ni catalyst showed quite high activity. In this study, CR of SS volatiles over Ni/Al₂O₃ can simultaneous decomposes the NO_x precursors and produces tar-free synthetic gas at 650 °C.

286 3.6.2. CSR

287 The nitrogen distribution during CSR of GSS volatiles was examined in a SPP of 30 kPa. As
288 shown in Fig. 6, nitrogen distribution from steam reforming is similar to that from non-steam and
289 non-catalytic reforming. Compared to CR, CSR of GSS volatile-N at 400 °C gives higher NH₃ and
290 N₂ yields. The presence of H₂O generally favors the formation of NH₃ during coal gasification [39].
291 As mentioned above, the activity of Ni/Al₂O₃ for NH₃ decomposition at 400 °C is quite low, and the
292 main reaction is CSR of the tarry materials in this temperature range. Thus, the increase of NH₃
293 yield at 400 °C should be due to the CSR of the tarry materials. H₂O also inhibit the destruction of
294 NH₃ even in the presence of O₂, due to the preferential adsorption of H₂O on the sites that would
295 otherwise catalyze the destruction of NH₃ [39]. Similar result was reported by Simell et al. [40] in
296 NH₃ decomposition over hot gas cleanup catalyst. In contrast, in this work, the NH₃ yield obtained
297 over CSR at 500 °C is lower than that of CR, suggesting that steam introduced promotes the NH₃
298 decomposition. Furthermore, CSR of the GSS volatiles above 550 °C gives a higher N₂ yield than
299 that of CR. Almost all the volatile-N was converted to N₂ in a yield of 77.4% at 650 °C. At the same
300 time, the nitrogen balance gets a good value of 100.4%. As explained in 3.2, some of the carbon
301 was found to be deposited on the catalyst surface and reactor wall during CR. This deposit-C might
302 decrease the activity of Ni/Al₂O₃ for NH₃ decomposition. The WGSR can significantly suppress the
303 carbon deposition and inhibit deactivation of nickel active sites. Therefore, the high conversion of
304 volatile-N to N₂ from CSR should be mainly related to the inhibition of carbon deposition in the
305 presence of steam.

306 3.6.3. Nitrogen transformation

307 As drawn in Fig. 7, Sludge-N was mainly converted to tar-N and NH₃ during pyrolysis, and
308 only small amount of nitrogen is retained as char-N. Subsequent thermal decomposition of
309 volatile-N at 650 °C is insufficient for complete conversion of volatile-N to N₂. CR of volatile-N
310 over Ni/Al₂O₃ primarily converted tar-N to NH₃ below 500 °C. At the same time, part of the HCN
311 evolved was converted to NH₃ (eq. 6), which then was catalytically converted to N₂ above 500 °C

(eq. 7). A part of the tar-N and HCN can be transformed to N₂ directly during CR of volatile-N. The nitrogen transformation depends strongly on temperature and atmosphere. It should be noted that more than 20% of nitrogen was retained as char-N, which could be released during further thermochemical utilization of the SS char. Understanding of the nitrogen transformation during gasification and combustion of SS char is a challenging work and deserves further investigation.

4. Conclusions

CR and CSR of the SS volatiles over Ni/Al₂O₃ at 650 °C successfully produced a tar-free synthetic gas and H₂-rich gas, respectively. The simultaneous reduction of NO_x precursors from gaseous products was also achieved at low temperatures. A high SPP and low SV is beneficial for H₂ production. The gas yield strongly depended on the sludge feedstock type. High carbon and hydrogen contents in SS facilitate the gas production. NO_x precursors in volatile-N cannot be completely converted to N₂ by the thermal cracking at the gasification temperature. As the main route for CR of volatile-N, tar-N was primarily cracked to NH₃, which was then completely decomposed to N₂. Future work will focus on the emission of sulfur, chlorine, and other harmful compounds along with assessment of the lifetime and reusability of the Ni/Al₂O₃.

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429 **Figure captions**

430 Table 1 Proximate and ultimate analyses (wt%) of the **SS** samples.

431 Table 2 Chemical composition of the **SS** ashes (expressed as wt% of metal oxides).

432 Figure 1 Schematic diagram of the two-stage fixed-bed system.

433 Figure 2 TG and DTG **curves** and gas yields from pyrolysis of GSS.

434 Figure 3 Effect of temperature on gas yields (a) and carbon distributions (b) from **CR** of GSS
435 volatiles.

436 Figure 4 Effects of **SPP** and SV on gas yields (a) and carbon distributions (b).

437 Figure 5 Gas yields from **CSR** of NSS and GSS **volatiles** at 400 and 650 °C in a **SPP** of 30 kPa and
438 **a SV of 4000 h⁻¹**.

439 Figure 6 Nitrogen distributions during **CR** and **CSR** of GSS **volatiles**.

440 Figure 7 Proposed nitrogen transformation routes during **CR** of SS volatiles.

Table 1Proximate and ultimate analyses (wt%) of the **SS** samples.

Sample	Proximate analysis			Ultimate analysis (daf)				$S_{t, d}$	H/C
	A_d	VM_{daf}	FC_{daf}	C	H	N	O [*]		
GSS	11.7	88.4	11.6	50.5	7.2	5.7	> 35.9	0.7	1.6990
NSS	21.4	82.1	17.9	55.8	8.2	9.4	> 25.3	1.4	1.7512

A: ash content; VM: volatile matter; FC: fixed carbon; d: dried basis; daf: dried and ash-free basis.
^{*} by difference.

Table 2

Chemical composition of the **SS** ashes (expressed as wt% of metal oxides).

Sample	CaO	P ₂ O ₅	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	ZnO	Others
GSS	31.0	20.2	22.0	12.5	7.8	3.0	2.2	0.7	0.7
NSS	21.8	19.8	24.33	11.9	10.8	5.6	1.9	0.9	3.0

Fig. 1. Schematic diagram of the two-stage fixed-bed system.

Fig. 2. TG and DTG curves and gas yields from pyrolysis of GSS.

Fig. 3. Effect of temperature on gas yields (a) and carbon distributions (b) from **CR** of GSS volatiles.

Fig. 4. Effects of **SPP** and SV on gas yields (a) and carbon distributions (b).

Fig. 5. Gas yields from CSR of NSS and GSS volatiles at 400 and 650 °C in a SPP of 30 kPa and a SV of 4000 h⁻¹.

Fig. 6. Nitrogen distributions during **CR** and **CSR** of GSS **volatiles**.

Fig. 7. Proposed nitrogen transformation routes during **CR** of SS volatiles.