1 Nitrogen transformation during gasification of livestock compost over transition metal and 2 Ca-based catalysts

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8 Abstract

9 Catalytic gasification of a pig compost (PC) was investigated over transition metal catalysts
10 (TMCs, including limonite, CoMo/Al₂O₃, Ni/Al₂O₃, and nickel loaded on lignite char) and
11 Ca-based catalysts (dolomite and CaO) in a two-stage fixed-bed reactor to understand the effects of
12 catalyst, temperature, and steam on nitrogen distributions. Non-catalytic thermal decomposition
13 (TD) of PC volatiles below 750 °C is not effective for decomposing the entire volatile nitrogen
14 species (VNSs) to N₂. NH₃ was found to be the predominant nitrogenous gas under **inert conditions**
15 **used in this investigation**, and its yield increased with raising TD temperature. The N yield in HCN
16 is lower than 5% below 550 °C, and sharply increased to 13.9% at 750 °C due to TD of volatiles.
17 Most of VNSs were converted to N₂ over TMCs, especially over Ni-based ones. The TMCs proved
18 to be quite active not only for tar reduction, but also for VNSs decomposition at 450-650 °C. On the
19 contrary, CaO-based catalysts, especially dolomite, significantly promoted the conversion of VNSs
20 to NH₃. Ni/Al₂O₃ effectively promoted the conversion of NH₃ and HCN to N₂ at 550 °C. Steam
21 introduced mainly prevented HCN decomposition over dolomite and coke deposition over Ni/Al₂O₃.
22 This study provides a basic insight into the nitrogen transformations during catalytic gasification of
23 PC, which would benefit the clean utilization of PC as an energy source.

24 **Keywords:** Pig compost; Gasification; Nitrogen transformation; Transition metal; NH₃; Ca-based
25 catalyst

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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 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 behaviours 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 $\text{Ni}/\text{Al}_2\text{O}_3$ (No. C13-4, Süd-Chemie Catalysts Japan, Inc., Ni loading 20 ± 2 wt.%, 0.5-1.0 mm) and $\text{CoMo}/\text{Al}_2\text{O}_3$ (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 M03XHF²² X-ray diffraction (XRD) and BELBELSORP-max constant volume adsorption apparatus were used for the catalyst characterization. The Ni loadings and Ni particle sizes (NPSs) in the $\text{Ni}/\text{Al}_2\text{O}_3$ and Ni/LYLC were determined as reported previously [16]. The main characteristics of the catalysts are shown in Table 3.

78 2.2. Gasification

79 CG was performed in a TSFBQR as reported previously [8]. The reactor tube (20 mm i.d. and
80 900 mm long) has two stages and is heated by two electrical furnaces, respectively. Argon was used
81 as the carrier gas with a flow rate of 120 mL/min. During the experiment, 1 g PC was put on the
82 first stage and 3 g catalyst was put on the second stage for catalytic decomposition of the tarry
83 species. When Ni/Al₂O₃, limonite, and CoMo/Al₂O₃ were used, the second stage was heated up to
84 650 °C for reducing the catalyst with H₂ for 1 h. After H₂ was replaced by Ar completely, the second
85 stage was set at a prescribed temperature between 450 and 750 °C. Then the first stage was heated
86 to 900 °C at 10 °C/min and held at that temperature for 0.5 h. The volatiles from PC pyrolysis were
87 streamed into the second stage for decomposition. For steam gasification, steam was fed through a
88 branch inlet, which was welded onto the main reactor at a position of 50 mm below the biomass
89 pyrolysis bed. When the first stage temperature reached to 100 °C, steam was generated and flowed
90 into the reactor for the PC volatile gasification at the second stage. Steam partial pressure in the
91 second stage was controlled at 30 kPa and the total flow rate of the feed gas was kept at 120
92 mL/min. The gaseous products (GPs) passed through two tar traps with deionized water (DIW)
93 cooled with an ice-water bath for water-soluble oil (WSO) collection, while the noncondensable
94 gases were collected in a gas bag for GC analysis. For the non-catalytic test, sand was put on the
95 second stage to the same bed height as the catalytic experiment. Soot deposited on the catalysts and
96 reactor wall was burned out at 600 °C under an O₂ flow rate of 80 mL/min for 1 h and collected in
97 another gas bag. When Ni/LYLC was used, the catalyst was moved out and only the soot deposited
98 on the reactor wall was determined.

99 2.3. Characterization

100 Total carbon and nitrogen contents in char recovered were determined with a Leco-2000
101 elemental determinator. H₂ and N₂ in GPs were analyzed with a Shimadzu GC/14B GC/TCD, while
102 the carbonaceous gases were analyzed with a Shimadzu GC/14B GC/FID equipped with a methane
103 converter to convert carbon oxides into detectable CH₄. Total organic carbon (TOC) and total

nitrogen (TN) contents in WSO were determined with a Shimadzu TOC-V_{CPH} TOC-TN analyzer. NH₃ and HCN absorbed in DIW were quantified with a TOA DKK ICA-2000 ion chromatograph as reported [12].

3. Results and discussion

3.1. Characteristics of the catalysts

As shown in Fig. 1, metallic nickel can be confirmed in Ni/LYLC by XRD analysis. Previous investigations [9,15] showed that the fine nickel particles dispersed quite well in Ni/LYLC. The average crystallite size of the nickel particles was obtained by Scherrer formula from the peak around 44 °. The NPSs of Ni/LYLC and Ni/Al₂O₃ was estimated to be 6.9 and 10.3 nm, respectively. In general, a higher NPS leads to a lower active surface/volume ratio and the decline in the activity of the NBC. In addition, Ni/LYLC has a higher BET surface area and a smaller pore size in comparison with Ni/Al₂O₃, as listed in Table 3. The results show that Ni/LYLC has a good textural characteristic and is expected to be active for CG. Limonite is regarded as an attractive alternative to the commercial Ni catalysts, due to the advantage in less expensive and abundant resource [13]. The limonite is mainly composed of goethite (FeOOH) with an iron content of 65.0% (expressed as metal oxides, as exhibited in Fig. 1 and Table 2). Iron oxide was converted to metallic iron after reduction at 650 °C. The BET surface area decreased from 149 to 46 m²/g, while the pore size increased to 16.6 nm, after reduction at 650 °C. The commercial CoMo/Al₂O₃ has CoO and MoO₃ contents of 3.0-4.0 wt.% and 13.0-15.0 wt.%, respectively. CoMo/Al₂O₃ has a relatively high surface area of 230 m²/g and can provide an enough reaction area, which is favorable for use in volatile reforming. As listed in Tables 2 and 3, the main component of the calcined dolomite is CaO, and this catalyst shows a mesopores characteristic with relatively low surface area. The calcined commercially available CaCO₃ was reported to possess more porosity in the range of mesopore region (2-50 nm) [17]. The CaO used in this study has a larger pore size and lower surface area in comparison with the calcined dolomite.

3.2. Non-catalytic test

As Fig. 2 shows, the nitrogen distribution, especially for NH₃ and HCN, is strongly affected by TD temperature. About 21.5% of nitrogen in PC (N_{PC}) was found to be retained in char (N_{char}), while the rest of the nitrogen was released as nitrogen in volatiles (N_{volatile}), which was found in the form of N_{tar}, NH₃, HCN, and N₂ (Eq. (1)).

NH₃, HCN, and N₂ were detected as the nitrogen-containing GPs and the yields of NH₃ and HCN increased with raising temperature via the reforming reactions (Eq. (2)), while no obvious change of N₂ yield can be found. NH₃ is the main NCSs under inert conditions used in this investigation. Even the second stage was set at room temperature (RT), significant formation of NH₃ (26.7% of N_{PC}) was observed. Pyrolysis of proteins as model compounds revealed that the composition of amino acids in proteins has a remarkable impact on the formation of NH₃ [18]. PC usually contains significant amount of proteins, most of which can be pyrolyzed at 400-500 °C [11]. Therefore, the formation of NH₃ should be related to its high protein content. The yield of NH₃ remained at a level in the temperature range up to 450 °C and then increased sharply to 37.9% by raising temperature to 650 °C. Further raising the temperature to 750 °C caused a decrease in the NH₃ yield to 30.5%. Similar result was reported for TD of NH₃ [19]. The yield of nitrogen in WSO (N_{WSO}) is quite low when the second stage was not heated. In this case, the nitrogen loss calculated by difference is ca. 31.8%, which should be in water-insoluble portion (WISP) or deposited in the reactor and is difficult to be detected. The N_{WSO} yield increased to 8.0% when the second stage was heated to 400 °C, slightly increased at 400-550 °C, and significantly increased to 12.6% at 750 °C. The tendency shows that TD at 400-550 °C mainly promotes the formation of N_{WSO} and NH₃.

The trend in the formation of HCN is different from that of NH₃. Below 550 °C, HCN yield is generally low (< 3.0% of N_{PC}), indicating that TD of PC volatiles at low temperatures cannot produce significant amount of HCN. HCN yield increased sharply to 13.9% by raising temperature to 750 °C. Similar trend was observed in waste pyrolysis [20,21]. Pyrolysis of thermally labile

156 nitrogen-containing aliphatic rings can produce methanimine (or can furnish such rings as
157 intermediates), affording relatively high yield of HCN. The temperature of 750 °C should be
158 favorable for decomposing such compounds.

159 Consequently, TD of PC volatiles below 750 °C is not effective for decomposing the entire
160 NH₃, HCN, and N_{tar}, all of which will be converted to NO_x and N₂O when the GP is used as fuel. A
161 proper catalyst is required for catalytic reforming (CR) of the volatiles and for reducing the NO_x
162 precursors.

163 3.3. Effect of TMCs

164 TMCs were widely investigated in biomass and coal gasification [13]. As can be deduced from
165 Fig. 3, the yields of carbon in char (C_{char}) over different catalyst are similar, which should be due to
166 the same pyrolysis temperature of 900 °C used. The TMCs are active for tar decomposition and
167 their activities at 650 °C decreased in the order: Ni/LYLC > Ni/Al₂O₃ > limonite > CoMo/Al₂O₃.
168 The higher activity of Ni/LYLC than Ni/Al₂O₃ is well consistent with the low NPS and high surface
169 area of Ni/LYLC. No carbon in WSO (C_{WSO}) was detected over limonite and NBCs, indicating that
170 all the tarry species from PC pyrolysis can be decomposed at 650 °C. However, 9.7% and 16.5% of
171 carbon were found to be deposited on the catalyst and reactor wall (C_{deposit}) over limonite and
172 Ni/Al₂O₃, respectively. Carbon deposition on the catalyst surface was reported to cover the active
173 sites, reduce the surface area, and lead to catalyst deactivation significantly [8]. It is necessary to
174 develop a strategy for avoiding the carbon deposition on the catalyst. Some carbon might also
175 deposit on Ni/LYLC, but it is difficult to determine this part of carbon due to the carbon supporter
176 of the Ni/LYLC. The catalytic activity of CoMo/Al₂O₃ for CR of PC volatiles is quite low in
177 comparison with limonite and NBCs, although CoMo/Al₂O₃ was reported quite active for
178 hydrodeoxygenation and upgrading of bio-oil [22]. In this case, the carbon balance is 98.4% and
179 1.0% of carbon is in the form of C_{WSO}. It can be confirmed that CoMo/Al₂O₃ mainly promotes the
180 formation of C_{deposit} (15.7%). Commercial CoMo/Al₂O₃ showed considerable activity for
181 decomposing natural gas to hydrogen and carbon nanotubes [23]. It is well known that Mo species

act as a promoter for methane aromatization at elevated temperatures [24]. The arenes produced can act as building units for the growth of carbon nanotubes on the active Co sites [24]. The carbon deposition on the catalyst may lead to the low activity of the CoMo/Al₂O₃ for PC volatile reforming.

The yield of N_{char} is lower than that of C_{char}, indicating that the release of N_{volatile} is more significant than that of carbon. The TMCs, especially NBCs, are active for converting N_{volatile} to N₂. NBCs proved to be quite active not only for tar reduction, but also for NH₃ decomposition (Eq. (3)) [8,13,25]. NBCs were reported to be active for decomposing NH₃ even at 400-600 °C [19]. At the same time, almost no HCN was detected, suggesting that NBCs are active enough for decomposing HCN. HCN can also be converted to NH₃ by subsequent reaction with H₂ (Eq. (4)) and decomposed to N₂ and C₂H₂ (Eq. (5)). In this study, almost all the NH₃, HCN, and N_{WSO} were converted to N₂ over Ni/Al₂O₃, while 92.6% of NH₃, 97.3% of HCN, and all the N_{WSO} were decomposed to N₂ over Ni/LYLC at 650 °C.

Limonite also shows a high activity for the conversion of N_{volatile} to N₂, which is consistent with catalytic decomposition of NH₃ [26] and nitrogen-containing heterocyclic compounds [27] over Fe-based catalysts. However, the nitrogen balance is 83.4%, which is lower than those over NBCs. Tsubouchi et al. [28] reported that metallic Fe formed from limonite achieved the almost complete decomposition of 0.2% NH₃ to N₂ at 500 °C. They suggested that the Fe-catalyzed NH₃ decomposition proceeded mainly through a cycle mechanism involving Fe metal and nitrides (Fe₃N and Fe₄N) (Eqs. (6) and (7)), and the decomposition of Fe nitrides into N₂ (Eqs. (8) and (9)) occurred below 700 °C. In this study, the limonite used contains large amount of Fe (65.0%, expressed as metal oxides, as exhibited in Table 2). The NCSs from PC pyrolysis might react with Fe to form Fe nitrides, which should not be completely decomposed at 650 °C, causing a relatively low nitrogen

208 balance.

213 CoMo/Al₂O₃ shows a moderate catalytic activity for converting NH₃ and N_{WSO} to N₂. However,
214 5.6% of nitrogen still remained in NH₃. Similar to carbon distribution, the nitrogen balance is as
215 low as 79.7%. The nitrogen lost when CoMo/Al₂O₃ was used should be in the form of WISP or
216 deposited on the catalyst. Compared with Ni- and Fe-based catalysts, CoMo/Al₂O₃ is less active for
217 tar reforming and NH₃ decomposition at 650 °C.

218 3.4. Effect of CBCs

219 CaO and dolomite can lead to tar reduction to a certain extent [29,30]. Both catalysts are active
220 for PC tar reduction, as shown in Fig. 3. The decrease in the carbon in gas (C_{gas}) was possibly due
221 to the reaction of CaO with the CO₂ in the GPs. C_{gas} was calculated by the sum of the carbon in the
222 carbonaceous gases, i.e., CO, CO₂, CH₄, and gaseous hydrocarbons from C₂ to C₄.

223 Different from the TMCs, CBCs are not so active for converting N_{volatile} to N₂. In contrast, the
224 NH₃ yield over the CBCs increased in comparison with that of non-catalytic experiment. As Fig. 3
225 illustrates, the CBCs significantly promote HCN and N_{WSO} decomposition. The NH₃ yield increased
226 from 38.0% during non-catalytic test to 43.8% and 62.8% over CaO and dolomite, respectively. The
227 results are well consistent with those reported by Leppälahti and colleagues [31], who stated that
228 dolomite was not active for NH₃ decomposition, but could reduce the HCN content via the reactions
229 of Eqs. (10) and (11) in the GPs. Dolomite was found to be less effective for NH₃ destruction during
230 coal gasification, but promoted the tar decomposition [30].

233 Although the calcined dolomite contains 96.7% of CaO, as exhibited in Table 2, its catalytic

activity is different from that of pure CaO. The catalytic activity of dolomite for decomposing HCN and N_{WSO} and producing NH_3 is higher than that of CaO. Therefore, dolomite is expected to be more active than CaO for PC tar decomposition. As listed in Table 3, the calcined dolomite processes a higher surface area and a smaller pore size, providing more reaction sites for the tar reforming in comparison with CaO. Other metallic oxides in dolomite may also catalyze the tar reforming to a certain extent. The N_2 yields obtained over the CBCs are higher than those without catalyst, indicating that the CBCs can also promote the conversion of N_{tar} to N_2 to a certain extent. Juutilainen et al. [32] found that dolomite is inactive for the conversion of NH_3 below 750 °C. In this study, the catalytic temperature was set to 650 °C, which is too low to decompose NH_3 .

3.5. Effect of temperature

$\text{Ni}/\text{Al}_2\text{O}_3$ and dolomite were employed to further study the effect of temperature on the nitrogen distributions. As shown in Fig. 4, almost neither HCN nor N_{WSO} was detected at 400-750 °C, suggesting that $\text{Ni}/\text{Al}_2\text{O}_3$ is active enough for decomposing N_{WSO} and HCN in this temperature range. The high activity of $\text{Ni}/\text{Al}_2\text{O}_3$ for HCN decomposition at 400 °C agrees well with the study by Osińska [33], who demonstrated that a nickel catalyst is active for decomposing HCN. The decomposition of N_{WSO} and HCN over $\text{Ni}/\text{Al}_2\text{O}_3$ at 400 °C mainly formed NH_3 , affording a higher NH_3 yield compared to non-catalytic test. However, the activity of $\text{Ni}/\text{Al}_2\text{O}_3$ for NH_3 decomposition is yet quite low at 400 °C. Wang et al. [19] also reported that the activity of a NBC for NH_3 decomposition was negligible at 400 °C. The NH_3 yield decreased sharply to 3.7% by raising temperature to 450 °C and then decreased to a negligible value above 550 °C. At the same time, the N_2 yield increased from 14.9% to 56.4% with raising temperature from 400 to 550 °C. The significant increase in N_2 yield at 400-450 °C is predominantly due to the NH_3 decomposition. Almost no NH_3 and HCN can be found above 550 °C, indicating that $\text{Ni}/\text{Al}_2\text{O}_3$ is active enough for NH_3 decomposition at 550 °C. The N_2 yield increased to 78.8% when further raising temperature to 750 °C. The main reaction in this temperature range should be the conversion of the nitrogen in WISP or deposited in the reactor form to N_2 . The results correspond to the previous studies on NH_3

decomposition from of coal and biomass pyrolysis over supported metals [8,13,25].

The trend in the nitrogen distribution over dolomite is different from that of Ni/Al₂O₃. Data in Fig. 5 show that NH₃ is the main NCSs in the temperature range of 450-750 °C. The NH₃ yield increased with raising temperature from 450 to 650 °C and decreased when further raising the temperature to 750 °C. Below 650 °C, dolomite mainly promoted the conversion of N_{WSO} to NH₃. The decrease in NH₃ yield at 750 °C should be due to the TD of NH₃ to N₂. Even at 450 °C, dolomite is quite active for reducing HCN. The result is well consistent with the study by Leppälähti and Kurkela [34], who reported that the CaO in dolomite can react with HCN to form NH₃. Since the NH₃ and HCN are value-added compounds, recovering rather than removing them is more favorable. Isolation of NH₃ as a pure compound during CR of PC volatiles over dolomite may significantly improve the economic feasibility of the PC gasification process.

3.6. Effect of steam

Steam is considered as an efficient method for large-scale H₂ production via the reaction of tar with steam and an effective strategy to prevent the carbon deposition and hence the catalyst deactivation. As can be deduced from Fig. 6, no obvious difference can be found between inert and steam reforming of PC volatiles without catalyst, indicating that feeding steam leads to little improvement on non-catalytic reforming of PC volatiles. Different from CR, CSR of PC volatiles over dolomite resulted in a high HCN yield of 4.4%. As mentioned in Section 3.4, dolomite is quite active for reducing HCN and negligible of HCN was produced during CR over dolomite at 650 °C. Such activity might be affected when steam was introduced. Park et al. [35] reported the suppression of HCN decomposition in the presence of steam for char-steam gasification. Similar to CR, almost all the N_{volatile} from PC pyrolysis was converted to N₂ over Ni/Al₂O₃. The N₂ yield obtained from CSR is higher than that from CR. As mentioned above, some of the N_{PC} was found to be deposited on the catalyst surface and reactor during CR. Such N_{PC} might be converted to N₂ by water–gas shift reactions. Therefore, the steam introduced mainly prevents HCN decomposition and carbon deposition over dolomite and Ni/Al₂O₃, respectively, at 650 °C.

286 3.7. Nitrogen transformation routes

287 As depicted in Fig. 7, the N_{PC} was mainly converted to N_{tar} and NH_3 during pyrolysis, and only
288 small amount of nitrogen is retained as N_{char} . The secondary thermal decomposition of $N_{volatile}$
289 mainly promotes the conversion of N_{tar} to NH_3 and the formation of HCN below and above 650 °C,
290 respectively. However, thermal decomposition of $N_{volatile}$ below 750 °C is insufficient for complete
291 conversion of $N_{volatile}$ to N_2 . During CG, TMCs primarily catalyzes the conversion of N_{tar} to NH_3 via
292 tar reforming reaction (Eq. (4)). Then the whole NH_3 undergoes a catalytic decomposition (Eq. (3))
293 and is subsequently converted to N_2 above 500 °C. The CBCs, especially dolomite, are active for tar
294 reforming and the conversion of the N_{tar} to NH_3 , but not effective for NH_3 decomposition. The
295 nitrogen transformation strongly depends on catalyst, temperature, and atmosphere. The activity for
296 CG over Ni/Al_2O_3 and dolomite can be significantly promoted when raising the temperature from
297 450 to 750 °C. The steam introduced can prevent the activity for HCN decomposition over dolomite
298 and carbon deposition on the NBC.

299 4. Conclusions

300 N_{PC} was mainly converted to NH_3 , HCN, N_2 , and N_{WSO} , and their yields increased with raising
301 temperature to 650 °C. NH_3 is the main nitrogenous gas under inert conditions used in this
302 investigation. TD at 750 °C mainly led to NH_3 decomposition and HCN formation. TD of the PC
303 volatiles below 750 °C is less effective for removing the entire NO_x precursors. TMCs, especially
304 NBCs, are quite active for converting $N_{volatile}$ to N_2 , while the CBCs, especially dolomite,
305 effectively catalyzed the conversion of $N_{volatile}$ to NH_3 at 650 °C. Ni/Al_2O_3 demonstrated excellent
306 activity for the decomposition of NH_3 and HCN to N_2 at 550 °C. Dolomite effectively improved the
307 conversion of HCN and N_{WSO} to NH_3 at 650 °C. Steam introduced mainly prevents HCN
308 decomposition and coke deposition over dolomite and Ni/Al_2O_3 , respectively.

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318 *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

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402 **Figure captions**

403 Table 1 Characteristics of the PC sample.

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

405 Table 3 Main characteristics of the catalysts.

406 Fig. 1. XRD patterns of the TMCs and CBCs.

407 Fig. 2. Effect of temperature on nitrogen distributions during TD of PC volatiles.

408 Fig. 3. Effect of catalyst on carbon and nitrogen distributions.

409 Fig. 4. Effect of temperature on nitrogen distributions over Ni/Al₂O₃.

410 Fig. 5. Effect of temperature on nitrogen distributions over dolomite.

411 Fig. 6. Effect of steam on nitrogen distributions over dolomite and Ni/Al₂O₃.

412 Fig. 7. Proposed nitrogen transformation routes during CG of PC volatiles.

Table 1

Characteristics of the PC sample.

Proximate analysis (wt.%, d) ^a			Ultimate analysis (wt.%, daf)				S _{t,d}	HCV
M _{ar}	A _d	VM _{daf}	C	H	N	O ^b	(wt.%)	(MJ/kg)
27.6	19.2	81.8	49.3	6.8	5.1	> 38.1	0.7	15.9

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 ₂ O ₃	SiO ₂	Al ₂ O ₃	NiO	Co ₂ O ₃	Cr ₂ O 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				96.7	0.32

Table 3

Main characteristics of the catalysts.

Catalyst	Average pore size (nm)	BET surface area (m ² /g)	Loading (wt.%)	NPS (nm)
Ni/Al ₂ O ₃	9.2	104	Ni: 20 ± 2	10.3
Ni/LYLC	3.0	348	Ni: 9 ± 1	6.9
Limonite	9.4	149		
Reduced limonite	16.6	46		
CoMo/Al ₂ O ₃	9.1	230	CoO: 3.0-4.0, MoO ₃ : 13.0-15.0	
Calcined dolomite	24.8	29		
CaO	37.6	11.6		
Sand	15.8	1.7		

Figure 1 color

Fig. 1. XRD patterns of the TMCs and CBCs.

Figure 1 (black and white)

Fig. 1. XRD patterns of the TMCs and CBCs.

Fig. 2. Effect of temperature on nitrogen distributions during TD of PC volatiles.

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Fig. 6. Effect of steam on nitrogen distributions over dolomite and Ni/Al₂O₃.

Figure 7 color

Fig. 7. Proposed nitrogen transformation routes during CG of PC volatiles.

Figure 7 black and white

Fig. 7. Proposed nitrogen transformation routes during CG of PC volatiles.