H₂ and syngas production from catalytic cracking of pig manure and compost pyrolysis vapor over Ni-based catalysts

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Catalytic cracking of volatiles derived from wet pig manure (WPM), dried pig manure and their compost was investigated over Ni/Al₂O₃ and Ni-loaded on lignite char (Ni/C). Non-catalytic pyrolysis of WPM resulted in a carbon conversion of 43.3% and 18.5% in heavy tar and light tar, respectively. No tar was formed when Ni/Al₂O₃ was introduced for WPM gasification and the gas yield significantly reached to a high value of 64.4 mmol/g at 650°C. When Ni/C was employed, 5.9% of carbon in the light tar was found at 650°C, revealing that the Ni/C is not active enough for cracking of tarry materials. The pyrolysis vapor was cracked completely and gave a H₂-rich tar free syngas in high yield. High water amount of WPM promotes steam gasification of char support, causing the deactivation of Ni/C. Such a study may be beneficial to the development of livestock manure catalytic gasification technology.

Keywords: Catalytic gasification, Pig manure, Compost, Ni-based catalyst.

INTRODUCTION

Livestock manure (LSM) is a kind of organic waste that is produced with an output of more than three billion tons from feedlots annually in China[1–3]. There are still lacking efficient solutions for the undesired and inevitable problems that LSM caused, such as unpleasant odors and water contamination[4]. In addition, it is a potential source of air pollution because of the emission of CO₂, NH₃, amides and other compounds during compositing process[5]. Land limitations and stringent regulations restricted the conventional disposal routes for LSM, such as agricultural application, landfill, and incineration[6]. It is urgent to develop an efficient and environment friendly technology to substitute the traditional ones for disposal of the waste.

As a typical biomass waste, LSM that contains high content of hydrocarbons can serve as a sustainable and renewable resource for high value-added utilization. Thermochemical technologies such as pyrolysis, gasification, liquefaction and biochemical conversion which convert biomass waste into high-grade liquids biochar and gas fuels have become more attractive[7–9]. Gasification is considered a promising way for the production of syngas (H₂ and CO) and H₂-rich gas among all the processes[10–14]. However, the most obstruction for the industrialization application of biomass gasification is related to tarry materials generally formed during the process. The undesirable tars condense downstream, causing process equipment blocking and corrosion. Catalytic gasification (CG) has been reported to be efficient for biomass tar cracking at moderate conditions and Ni-based catalysts are widely used for hot gas cleaning[15–18]. CG of LSM at low temperatures has been studied[5, 19]. LSM undergoes decomposition at high temperature and the pyrolysis volatiles passed through the catalyst bed and were converted into H₂, CO, CO₂, and other small molecular compounds. But above all, there is rarely reported about the release behavior of LSM under different catalysts,

nickel contents, catalytic temperatures (CTs) and feedstock during CG process in detail.

LSM that possesses high content of water is generally pretreated by dehydration before it is fed into gasifier. During gasification process, moisture evaporation usually consumes considerable heat. Previous studies on LSM gasification focused on the dried samples[5, 19]. The presence of moisture might influence catalytic activity. Therefore, understanding the catalytic performance at absence/presence of moisture is necessary for the application of LSM low-temperature gasification.

Catalytic cracking of LSM pyrolysis volatiles was investigated over a pre-prepared Ni-based catalyst, i.e., a commercial Ni/Al₂O₃ and Ni-loaded on lignite char (Ni/C) in a two-stage fixed-bed quartz reactor. The effects of nickel content, CT and feedstock on carbon distribution and gas production were investigated.

EXPERIMENTAL

Material

Wet pig manure (WPM) and its dried compost, namely dried pig compost (DPC) were obtained from a piggery in the Gunma Prefecture, Japan. WPM was dried at 107°C overnight to prepare dried pig manure (DPM). The powdered LSMs with a particle size of 0.5–1.2 mm were used as feedstock. The moisture content in WPM was determined by a KEM ADP-512S evaporator and a KEM MKA-610 Karl-Fischer moisture titration. The proximate and ultimate analyses of LSMs were reported previously[20].

Commercial Ni/Al₂O₃ (No. C13-4, Süd-Chemie Catalysts Japan, Inc., Ni content 20 ±2 wt%, 0.5–1.2 mm) and Ni/C catalyst (Ni content 19 ±1 wt%) were employed for CG. Nano-sized crystals embedded were identified and the nickel species distribution on the support materials was investigated and the characterization results were reported previously[21, 22].

Instrument analysis

Major phases on catalysts were collected by a Mac Science M03XHF X-ray diffraction (XRD) with Cu Kα radiation at 40 kV and 30 mA, which have a scanning speed of 1°/min from 10 to 110°. A JEOL JEM-2010 transmission electron microscope (TEM) was employed for the catalyst characterization, and ultrasonic washer was employed to achieve a finely pulverization and dispersion of catalyst in ethanol. Observations were made at random places and image were obtained at a magnification of 50000 to 15000 times. Brunauer-Emmett-Teller (BET) surface area of catalysts were carried out at 77 K using a Quantachrome Autosorb-1 instrument for the determination of SSA (multipoint BET method) and pore size distribution.

Gasification and product analyses

The schematic diagram of TSFBQR was reported previously[21]. During CG process of LSMs Ar of 120 mL/min was used as carrier gas and the space velocity was stabilized at 3500 h^{-1}. Firstly, 5 g of sample was placed in the first stage while the catalyst was in the second. After air-tightness examination, the catalyst was firstly programmed up to a prescribed CT ranging from 650 to 750°C at 10°C/min. If Ni/Al$_2$O$_3$ was used, it was reduced in H$_2$ for 0.5 h at a reduction temperature of 650°C. Secondly, the sample was heated at 10°C/min to the final decomposition temperature of 900°C and maintained for 0.5 h. For non-catalytic test, inert sand with a same height substitutes the catalyst for CG.

The pyrolysis volatiles passed through the catalyst bed and some of them condensed on the quartz wool at the bottom of the reactor and collected as heavy tar. Ice-cooled traps containing deionized water for light tar collection while the non-condensable gas products (GPs) were collected by a gas bag.

Total organic carbon (TOC) in deionized water was detected using a Shimadzu TOC-VCPH TOC analyzer through two-stage processes involving combustion and detection. The GPs were analyzed by a Shimadzu GC/14B gas chromatograph (GC) equipped with TCD for the analysis of H$_2$ and a Shimadzu GC/14B GC equipped with FID and methane converter for the analysis of carbonaceous gases. The carbon amount of coke deposited on Ni/Al$_2$O$_3$ and quartz tube was measured by the amount of CO$_2$ formed during the combustion at 600°C in 80 mL/min O$_2$. If Ni/C was employed, the catalyst was removed and only the carbon deposition on the quartz tube was measured. The amount of carbon in char recovered was measured with a Leco-2000 elemental analyzer.

RESULTS AND DISCUSSION

Characterization of catalyst

XRD analysis

Significant Ni peaks in XRD patterns (Figure 1) of the Ni/Al$_2$O$_3$ and Ni/C was observed. Two of Ni-based catalysts exhibited small reflections at 2θ of 44.5°, 51.7° and 76.3°, which were attributed to the (111), (200) and (220) planes of Ni, respectively[23–25]. Furthermore, no broader diffraction peaks of NiO for the Ni/C and Ni/
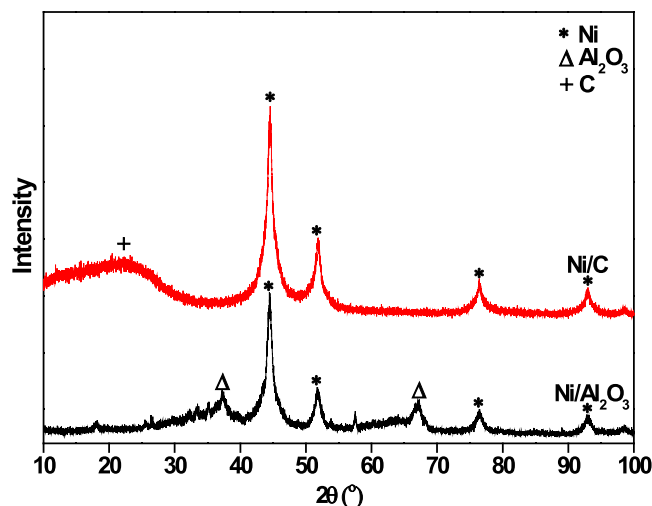

Figure 1. XRD patterns of the Ni/Al$_2$O$_3$ and Ni/C

Al$_2$O$_3$ can be observed, suggesting the complete reduction of Ni in the commercial Ni/Al$_2$O$_3$. Ni metal in Ni/C was reduced by H$_2$ and CO produced by lignite pyrolysis. Ni crystallite size (NCS) is also confirmed by the Jade software and Scherrer formula, which were listed in Table 1. Generally, a relatively low NCS of catalyst will have a high activity for WPM and DPM cracking. Ni/Al$_2$O$_3$ and Ni/C, with the lowest NCS of 10.3 and 6.9 nm were applied to catalytic cracking of pig manure. At the same time, the XRD pattern shows the lowest intensity of the major peaks and NCS, which demonstrates the decrease of the degree of crystallinity.

TEM analysis

TEM images of Ni/C and Ni/Al$_2$O$_3$ catalyst were shown in Figure 2. TEM analysis highlights the presence of nickel embedded in the support. The average Ni diameter of Ni/C and Ni/Al$_2$O$_3$ are narrow within 6.8 nm and 10.1 nm. The results are comparable to the NCS obtained from XRD analysis. In particular, TEM micrograph of Ni/C highlight the presence of nickel nanoparticles embedded in the carbon carrier. The uniformly dispersed nano Ni particles on the carrier making it beneficial for the CG reaction. In conclusion, the TEM images imply that Ni/C and Ni/Al$_2$O$_3$ have a great Ni dispersion and small metallic Ni particle[26], which is expected to provide a high activity for pig manure cracking.

BET analysis

From the classification of the IUPAC[27], the adsorption isotherms of the two catalysts are consistent with the combination of type I and type II. Ni/C shows an obvious microporous characteristic, and Ni/Al$_2$O$_3$ shows the characteristic of mesopores, which can be concluded from the p/p_0 of the Figure 3. The steep absorption peak at p/p_0 above 0.1 shows the presence of mesopores and macropores. From the Figs. 2, 3 and Table 1, it can be easily observed that Ni/C catalyst has the smallest pore size of 1.8 nm. The SSA of Ni/Al$_2$O$_3$ reached to the maximum value of 104 m^2/g. The Ni/C presents larger SSA (348 m^2/g) than Ni/Al$_2$O$_3$ catalyst, and can be used as the potential high activity biomass gasification catalyst.
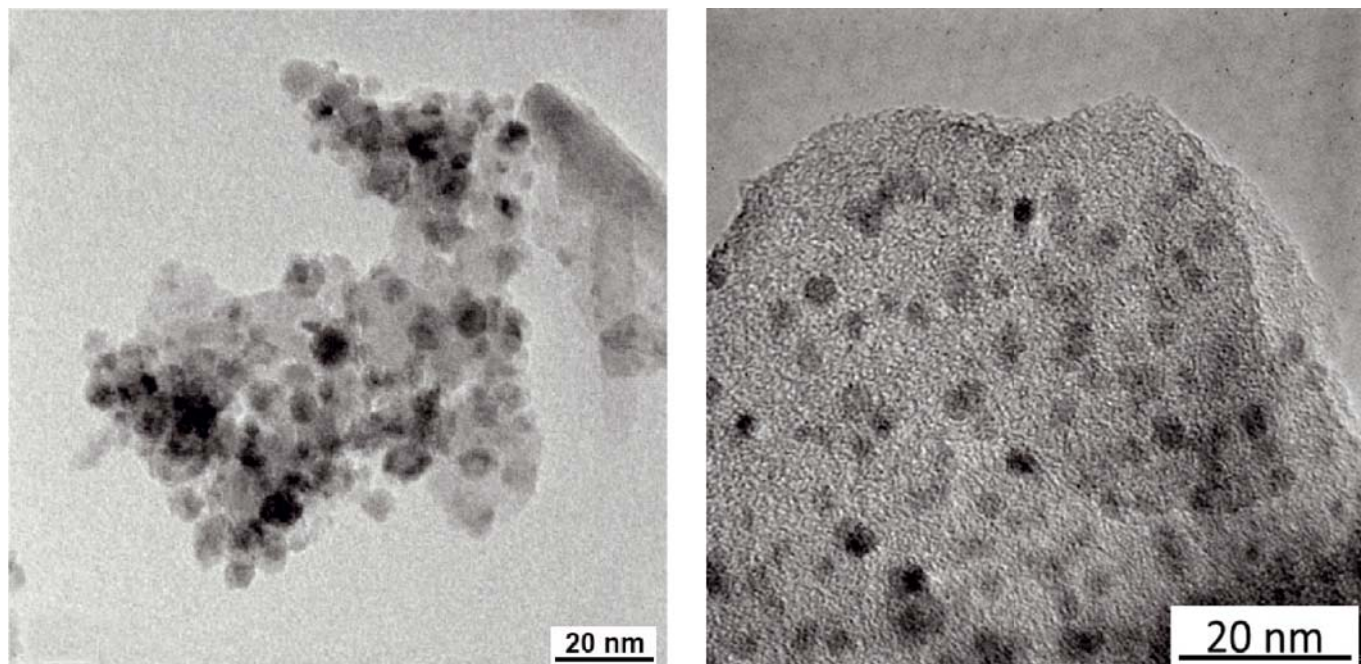
Figure 2. TEM images of Ni/Al$_2$O$_3$ and Ni/C
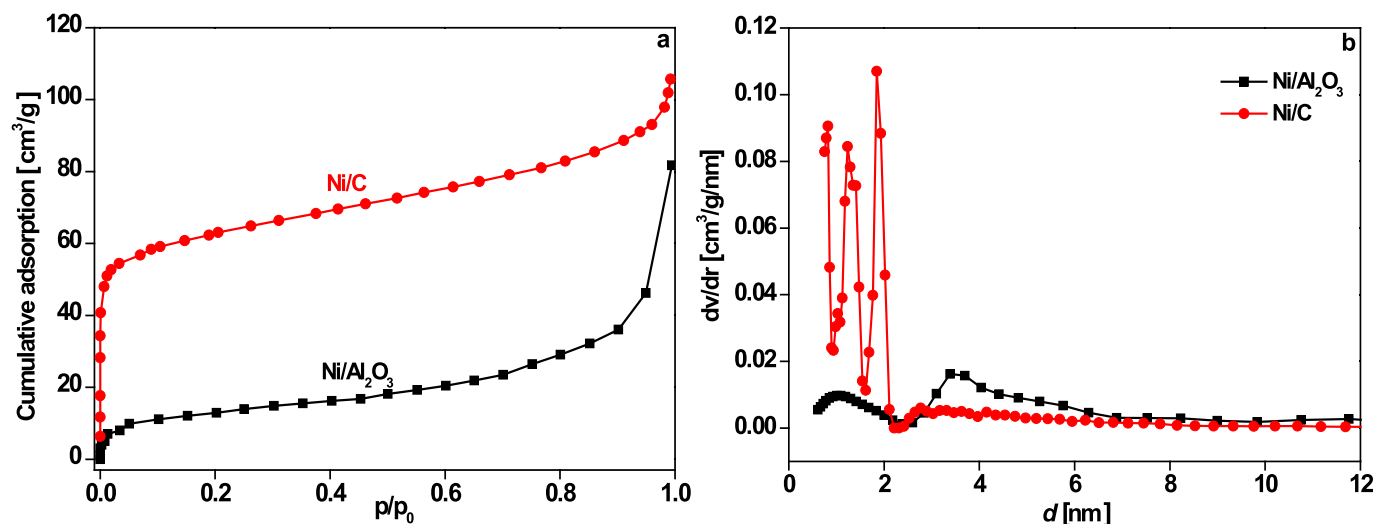
Figure 3. Nitrogen adsorption isotherms (a) and pore size distributions (b) of Ni/Al$_2$O$_3$ and Ni/C

**Table 1.** Main characteristics of the Ni/Al$_2$O$_3$ and Ni/C

Catalyst	D_a [nm]	SSA [m^2/g]	NCS [nm]	TPV [cm^3/g]
Ni/Al$_2$O$_3$	10.9	104	10.3	0.13
Ni/C	3.0	348	6.9	0.16

D_a: average Ni diameter

Effect of catalyst

Carbon distribution

Nickel-based catalyst was reported to exhibit considerable activity for tar removal at mild conditions and was widely used in biomass gasification[28, 29]. The catalytic performance of Ni/C and Ni/Al$_2$O$_3$ was investigated in WPM gasification at the CT of 650, 700 and 750ºC. As shown in Figure 4, for non-catalytic pyrolysis of WPM, 24.1% of carbon in WPM (C_{WPM}) was found to be retained in char. Only 14.4% C_{WPM} was transferred into gases while 55.7 % of carbon in tar (C_{tar}) was found. C_{tar} can be divided to 15.3% of carbon in light tar (C_{LT}) and 40.4% of carbon in heavy tar (C_{HT}) when WPM cracking without catalyst. It indicates that non-catalytic thermal decomposition of WPM is not an applicable option in terms of gas production.
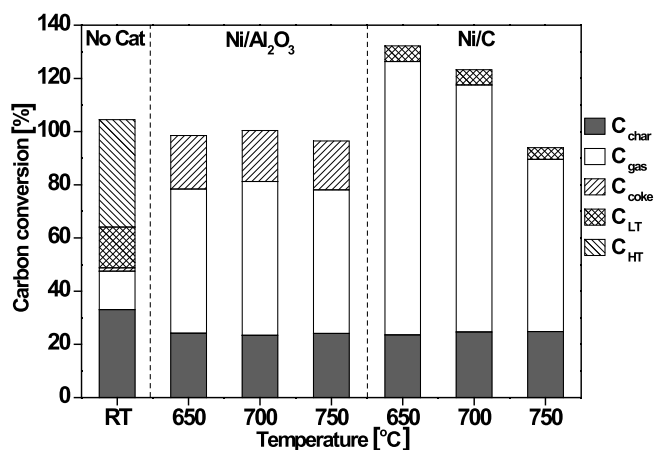
Figure 4. Effect of temperature on carbon conversion over Ni/Al$_2$O$_3$ and Ni/C

As expected, Ni/Al_2O_3 and Ni/C dramatically promote the decomposition of manure volatiles. Ni/Al_2O_3 showed excellent activity for tar removal and gas reduction. No tar was detected in deionized water and the carbon in gas (C_{gas}) increased remarkably compared with that of non-catalytic test. It is due to the conversion of tarry materials and hydrocarbon compounds into H_2 and other low-molecular weight carbonaceous gases when the WPM volatiles passed through the catalyst bed. However, the carbon of coke deposited (C_{coke}) on Ni/Al_2O_3 is as high as 20.1% at 650°C. This finding was in high conformity with previously report[30–33]. The primary drawback of Ni/Al_2O_3 lies in coke deposition on its surface and leading to rapid deactivation. When further increasing CT to 750°C, C_{coke} slightly decreased while C_{gas} conversely increased, which should be attributed to the decomposition of coke at a higher temperature above 650°C.

The carbon distribution over Ni/C was quite different from that over Ni/Al_2O_3. When CG over Ni/C, C_{gas} was higher than that of Ni/Al_2O_3. Besides, the carbon balance over Ni/C reached to 132.7% at 650°C, which is caused by the gases derived from lignite char steam gasification[20]. The amount of coke deposition on carbon based catalyst is difficult to be calculated accurately. Therefore, C_{coke} was not considered in the case where Ni/C was employed for CG. Compared with the result of non-catalytic test, Ni/C shows certain activity for tar reforming, but there are still 5.9% of C_{LT} at 650°C. It reveals that Ni/C was not active enough for complete tar removal. With the CT rising from 650 to 750°C the carbon balance decreased to 93.3% and C_{gas} decreased from 102.7% to 64.8%, which indicates the decline in the activity of Ni/C. As reported, the high temperature above 650°C will cause nickel particle agglomeration on the surface of carbon and inhibits the catalytic activity of Ni-based carbon catalyst[34]. In addition, the low activity of Ni/C is also related to the high content of water, which resulted in steam gasification of Ni/C and its deactivation[19].

Gas composition

The GPs are the most predominate products derived from manure pyrolysis or gasification, which can serve as versatile energy carrier for direct use or a feedstock for synthesis of clean transportation fuels. The gas composition from WPM gasification over Ni/Al_2O_3 and Ni/C is shown in Figure 5, from which H_2, CO and CO_2 are found to be the main GPs in all cases. In addition, a small amount of gaseous products with carbon atoms between 2 and 4 (C_2-C_4) were also detected. The total gas yield increased significantly in the presence of Ni-based catalyst, especially the yield of syngas (H_2 and CO). The syngas yield is 9.96 and 16.42 times higher for Ni/Al_2O_3 and Ni/C than that of non-catalytic test at 650°C. The remarkable increase of syngas is related to a series of enhanced reactions by the catalysis of metallic Ni, such as water-gas-shift reaction, char gasification and steam reforming of tar[35]. In contrast to Ni/Al_2O_3, the syngas yield decreased over Ni/C with the CT rising from 650 to 750°C, which is caused by the decline in the activity of Ni/C.
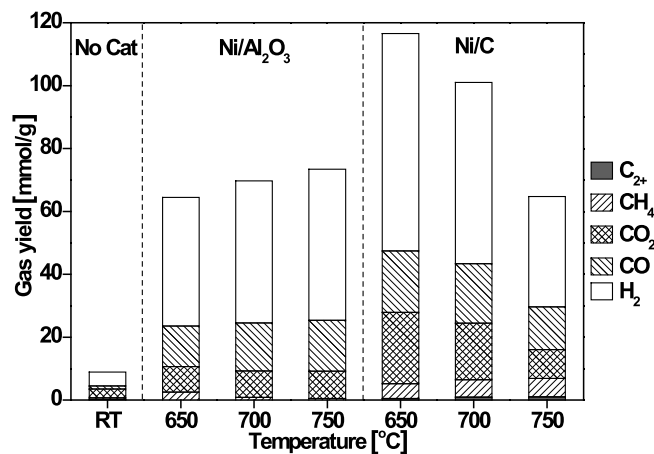

Figure 5. Effect of temperature on gas yield over Ni/Al_2O_3 and Ni/C

Effect of moisture in WPM

The gasification of DPM over Ni/C was carried out to study the influence of moisture on the catalytic performance of Ni/C. As shown in Figure 6, 2.0% of C_{LT} was found in DPM gasification at 650°C, which is lower than that in WPM gasification. The result reveals that moisture causes the deactivation of Ni/C and restrains catalytic cracking of manure pyrolysis volatiles. The higher C_{gas} in WPM gasification than that in DPM gasification is due to steam gasification of char support by the catalysis of the inside dispersed nickel species[22]. Tomita et al. also suggested that well-dispersed nickel particles exhibited good catalytic performance for steam gasification of lignite[36]. When increasing CT to 700°C, C_{LT} reaches a high value of 8.6%, 4.32 times higher than that at 650°C, indicating the temperature is a primary factor limiting the activity of Ni/C.
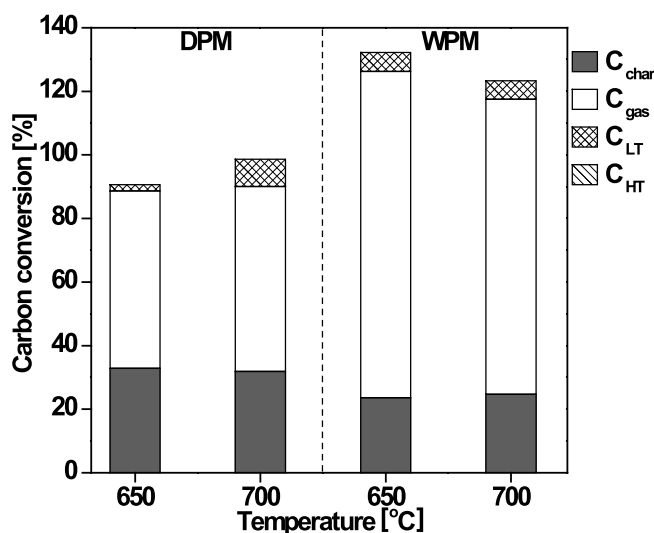

Figure 6. Effect of moisture on carbon conversion over Ni/C

Effect of nickel content

The nickel amount is calculated to be 1.57 and 0.5 g for Ni/Al_2O_3 and Ni/C, respectively in foregoing gasification tests. The lower catalytic activity of Ni/C in WPM gasification than Ni/Al_2O_3 is probably attributed to the low amount of nickel in the supporting material. Therefore, Ni/Al_2O_3 with 0.5 g and 1.57 g of Ni was employed for WPM gasification to investigate the influence of nickel content on carbon conversion and GPs. The results are

shown in Figures 7 and 8. In contrast to Ni/C, when 0.5 g and 1.57 g Ni was used for WPM gasification, the gas yield have a tendency to increase with increasing temperature. Compared with 1.57 g Ni of Ni/Al$_2$O$_3$ at 650°C, 0.5 g Ni produced 2.1% of C_{LT} in the WPM gasification at 650°C and the C_{gas} decreased from 54.2% to 49.5%. It indicates a decline in the catalytic activity compared with 1.57 g Ni. But compared with Ni/C with 0.5 g Ni, Ni/Al$_2$O$_3$ with same Ni amount shows higher activity in terms of tar formation. When 0.5 g and 1.57 g Ni of Ni/Al$_2$O$_3$ was used, the total gas yield increased by 4.46 and 8.96 mmol/g from 650 to 700°C, respectively. It indicates that high temperature can promote the decomposition of WPM volatiles to GPs. In addition, the carbon conversion and total gas yield are shown in Figures 7 and 8, which are lower than those with 1.57 g of Ni. Therefore, small nickel content in Ni/C may result in the low activity for tar cracking during WPM catalytic gasification.
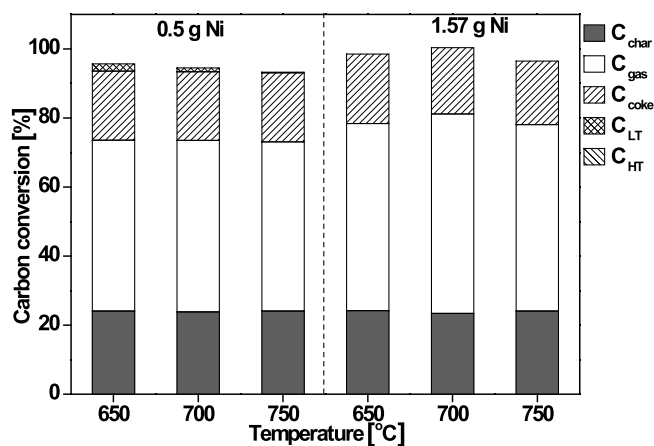
As Figure 9 shows, the carbon in char (C_{char}) is 38.3%, which is higher than that in WPM and DPM gasification. On the contrary, C_{gas} decreased from 54.5% to 50.6% at 650°C and from 53.7% to 48.7% at 700°C compared with WPM gasification. The increased C_{char} and the decreased C_{gas} in DPC gasification are mainly due to the loss of carbon containing species. It reported that large amounts of carbon were removed due to the decomposition of instable carbon containing species during the composting process[37]. Moreover, as composting progressed, stable carbon compounds were formed which were less susceptible to volatilization, decarbonation, and leaching[38]. The loss of carbon containing species during the composting process also caused the decrease of syngas yield. As shown in Figure 10, the syngas yield from DPC gasification is 48.0 mmol/g at 650°C and 49.7mmol/g at 700°C, which is lower than that in WPM gasification. As expected, no C_{LT} and C_{HT} was found in DPC gasification, suggesting that Ni/Al$_2$O$_3$ has the potential for low-temperature cracking of tar materials from LSM pyrolysis.

Figure 7. Effect of nickel amount on carbon conversion over Ni/Al$_2$O$_3$
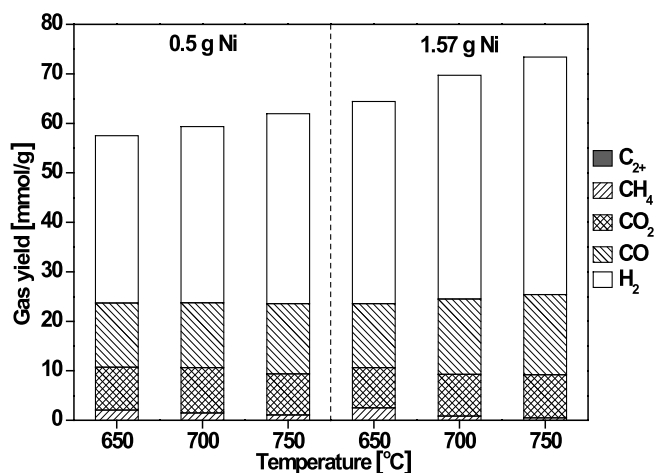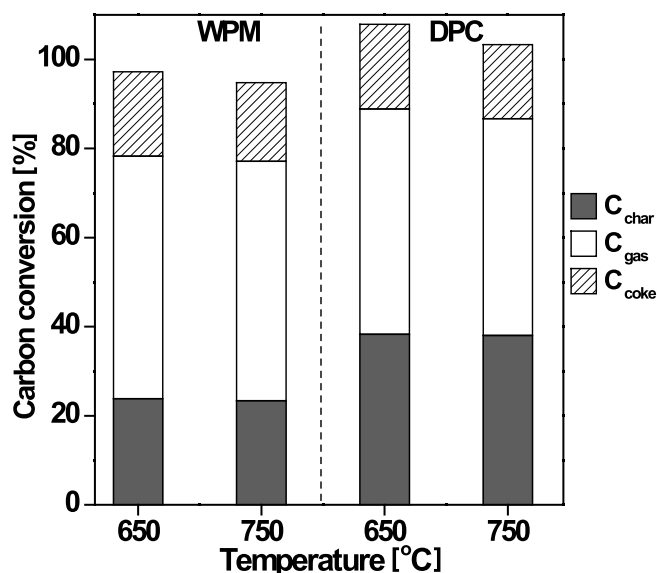

Figure 8. Effect of nickel amount on gas yield over Ni/Al$_2$O$_3$

Effect of feedstock type

The larger amounts of ash and fixed carbon in DPC than those with WPM reported previously is caused by the degradation of organic matter and the residual of bacteria during compost process that LSM usually undergoes[19]. It is believed that the composting process will certainly influence the catalytic decomposition of LSM pyrolysis volatiles. The DPC gasification over Ni/Al$_2$O$_3$ was also carried out to study the effect of composting process.

Figure 9. Effect of feedstock on carbon conversion over Ni/Al$_2$O$_3$
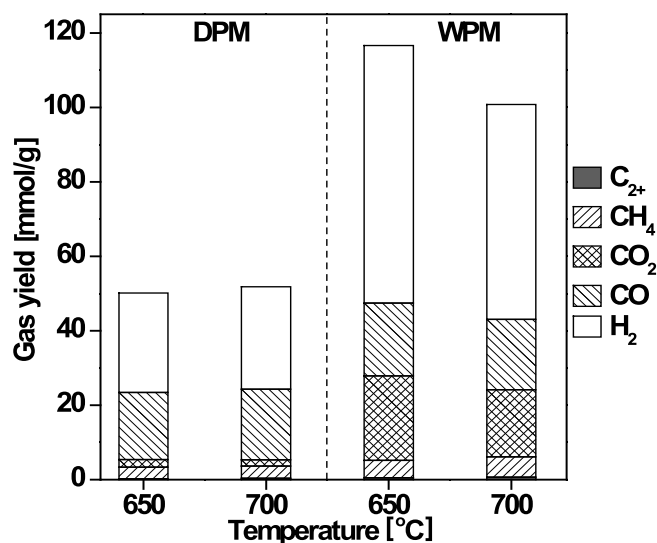

Figure 10. Effect of feedstock on gas yield over Ni/Al$_2$O$_3$

CONCLUSIONS

Commercial Ni/Al_2O_3 and prepared Ni/C showed high activity in the decomposition of tarry materials. The total gas yield of WPM gasification at 650°C increased 7 and 13 times for Ni/Al_2O_3 and Ni/C relatively, which were higher than that from non-catalytic test. No tars were formed for Ni/Al_2O_3 and only 5.9% of C_{LT} was found in Ni/C at 650°C. High temperature above 650°C increased the catalytic activity of Ni/Al_2O_3 but caused the decline of catalytic activity of Ni/C. High water content of WPM, which can promote the steam gasification of char support, also caused the deactivation of Ni/C. More than 0.5 g of Ni were required for complete removal of tarry materials. For DPC catalytic gasification, more C_{char} and less C_{gas} yield were obtained compared with WPM, suggesting that more stable carbon species were formed during the composting process.

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