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# Conversion of nitrogen compounds and tars obtained from pre-composted pig manure pyrolysis, over nickel loaded brown coal char

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## ARTICLE INFO

### Article history:

Received 5 April 2011

Received in revised form

6 April 2013

Accepted 28 May 2013

Available online 27 June 2013

### Keywords:

Pig manure

Catalytic decomposition

Nitrogen transformation

Nickel-loaded brown coal

Light fuel gas

## ABSTRACT

Fuel gas production and nitrogen transformation during pig manure pyrolysis from room temperature to 900 °C are investigated. The catalytic decomposition of the derived volatiles is also studied. Ammonia, HCN and N<sub>2</sub> were obtained as the main N-containing gases. Ammonia was mainly emitted below 700 °C, which corresponds to 24.8 wt% of the nitrogen in the manure. Hydrogen cyanide and N<sub>2</sub> gases obviously formed at temperatures above 700 °C, while the HCN concentration was as low as one ninth that of NH<sub>3</sub> and one fifth of the concentration of nitrogen even at 900 °C. Thermal cracking of the pyrolysis volatiles produced little NH<sub>3</sub>, but noticeably increased HCN formation.

When the prepared nickel-loaded brown coal char (LY-Ni) was added to the second part of the reactor (second stage) as a catalyst, most of the N-containing species in the volatiles converted into N<sub>2</sub> gas. It suggests that LY-Ni has high catalytic activity for the conversion of N-containing compounds. Significant quantities of light fuel gases (H<sub>2</sub>, CO and CH<sub>4</sub>) were also generated. Compared with sand, 5.8 times (H<sub>2</sub> and CO) the amount of gases was produced with the LY-Ni char at 650 °C. Decomposition of the manure volatiles depends on the catalyst temperature. Total product gases approximately doubled in yield when the catalyst temperature increased from 450 to 550 °C, and the volatiles conversion (based on carbon balance of the manure volatiles) increased from 72.4 wt% to 92.0 wt%. At 600–700 °C, the volatiles conversions stabilized at high levels of 96.7–98.2 wt%.

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## 1. Introduction

With chemical fertilizer application and increased meat consumption, excessive livestock waste is produced in many countries. Ninety million tons of livestock manure is produced annually in Japan [1]. Storing the waste in fields causes environmental problems, such as unpleasant odors and water contamination, and air pollution occurs from the emission of

greenhouse gases, NH<sub>3</sub>, amides and other compounds [2]. With concerns over environmental pollution and regulatory constraints, adequate treatment for livestock waste is required. With respect to global issues of sustainable energy and greenhouse gas reduction, more attention is being paid to biomass wastes as potential sources of renewable energy.

Regarding biomass waste-to-energy research, various technologies have been developed. Sweeten et al. proposed a

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<http://dx.doi.org/10.1016/j.biombioe.2013.05.028>

co-firing technology using animal waste (cattle feedlot) and coal in different boiler burner facilities [2–4]. Considering that livestock wastes have low energy densities, high ash and water contents, much attention has been paid to thermochemical conversion technologies. Ro et al. [5,6] reported that high heating value (HHV) gases were produced from pyrolysis of animal manures at 620 °C. The value-added swine-based bio-char, containing approximately 50% of feedstock energy, had HHVs between that of high and low rank coals. Priyadarsan et al. [7] and Hamel et al. [8] focused their attention on biomass gasification. Fuel gases or synthesis gases are generated from the gasification process, which are expected to reduce the dependence on fossil fuels as well as decreasing greenhouse gas emissions. However, during biomass pyrolysis/gasification, tarry materials generally form as by-products. The tar condenses and can block and foul process equipment when pipe temperatures are lower than the tar dew point. Livestock wastes have high nitrogen content. N-containing compounds such as NH<sub>3</sub>, HCN and HNCO are produced in gasification processes [9] and convert into NO<sub>x</sub> when they are combusted in e.g. a gas engine or turbine. Therefore, tar disposal as well as, the scrubbing of these NO<sub>x</sub> precursors is necessary.

Biomass-derived tar is hard to crack by thermal treatment alone [10]. Brandt and Henriksen found that a high temperature of 1250 °C was necessary for tar to completely decompose [11]. High-temperature operation increases operating costs and decreases energy efficiency. Biomass tar destruction should be realized at more moderate temperatures using appropriate catalysts. The activities of Ni-based catalysts, calcined dolomites and magnesites, zeolites, olivine and iron catalysts have been extensively investigated for biomass tar catalytic decomposition [12]. Supported Ni catalysts are highly effective in tar decomposition/cracking [13,14]. Wang et al. reported that Ni-based catalysts are effective for NH<sub>3</sub> decomposition when the catalyst temperature is above 800 °C [15]. Pinto et al. and Simell et al. observed that nickel catalysts are effective for NH<sub>3</sub> decomposition as well as tar reduction at 900 °C [13,16].

Commercial Ni catalysts are expensive, and the manure gasification process is not cost-effective when using these high-cost catalysts. In this work, we focus on catalyst development using brown coal as a catalyst support, as it is geographically distributed, is available at low cost and has certain structural properties. The abundant O-containing (acidic) functional groups in brown coal act as ion-exchangers for metal ions, resulting in well dispersed metal ions in the coal matrix [17]. In nickel-loaded brown coal char, nickel particles disperse well, with particle sizes in the nanometer range [18,19]. The ion-exchanged nickel species have high activity in steam gasification of the brown coal matrix at temperatures of about 600 °C [18,20–22]. Because of the low price of brown coal, the catalyst recovery process could be omitted. At the end of service life, the catalyst can be disposed of simply by gasifying or burning coal char, during which the energy value of the coal char can be recovered. Agglomerated nickel residue can also be used as a functional material in powder metallurgy and battery development. In our latest study we showed that the cracking of hydrocarbons produced very little carbon deposits on nickel-loaded coal char,

compared with a commercial Ni/Al<sub>2</sub>O<sub>3</sub> catalyst [23]. We therefore investigate the catalytic behavior of nickel-loaded brown coal char on biomass waste gasification.

In this study, the pyrolysis of pre-composed pig manure was conducted in a two-stage fixed-bed reactor. The influence of nickel-loaded brown coal char on the conversion of the manure volatiles and N-containing compounds was investigated.

## 2. Material and methods

### 2.1. Sample preparation and experimental conditions

Pig manure underwent a typical composting process where organic materials and volatile nitrogen in the manure are stabilized, odors are reduced and pathogens are destroyed. The composting process also reduced the water content and the waste volume to improve transportability and operability [24]. The manure sample, in the form of granular pieces (<2 mm), was easily fed into a gasification system without sticking. The composition of the pre-composed pig manure is listed in Table 1.

Loy Yang brown coal (LY; Victoria, Australia; 0.5–1.0 mm) was used for nickel-loaded coal preparation. The LY coal composition is shown in Table 2. To prepare the catalyst, coal was impregnated with ammonia, aqueous solution (pH = 11) of hexamine nickel (II) carbonate using a previously reported method [25]. The nickel-loaded LY coal (LY-Ni, Ni: 9.2 wt%) was de-volatilized in a flow of nitrogen from ambient temperatures to 600 °C at 20 °C min<sup>-1</sup> and held at 600 °C for 30 min to produce LY-Ni char. The nickel content of the LY-Ni char was 17.0 wt%.

Pig manure pyrolysis and subsequent volatile decomposition were carried out in a two-stage fixed-bed reactor [26] (Fig. 1). The second stage is filled with the nickel catalyst or sand and preheated at 20 °C min<sup>-1</sup> to the desired reaction temperature, to decompose the manure volatiles. The manure sample (approximately 1 g) is heated from ambient temperature to 700 °C at a rate of 10 °C min<sup>-1</sup> in the first stage. The pyrolysis volatiles were transferred into the second stage in argon carrier gas (gas velocity: 2 cm s<sup>-1</sup>), where the gas residence time in the catalyst bed was 1 s.

### 2.2. Analytical methods

A thermogravimetry analyzer (TGD-9600s, ULVAC-RIKO, Inc.) measured the mass loss of the pig manure (0.1 g for each run),

**Table 1 – Proximate and ultimate analyses of pre-composed pig manure.**

Proximate analysis (wt%)				Ultimate analysis (wt%, daf <sup>a</sup> )				
Mois.	V.M.	F.C. <sup>b</sup>	Ash	C	H	N	S	O <sup>b</sup>
24.5	54.0	9.7	11.8	49.4	7.4	3.9	0.6	38.7
a daf: dry ash free basis.								
b By difference.								

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