



## Carbon dioxide assisted thermal decomposition of cattle excreta



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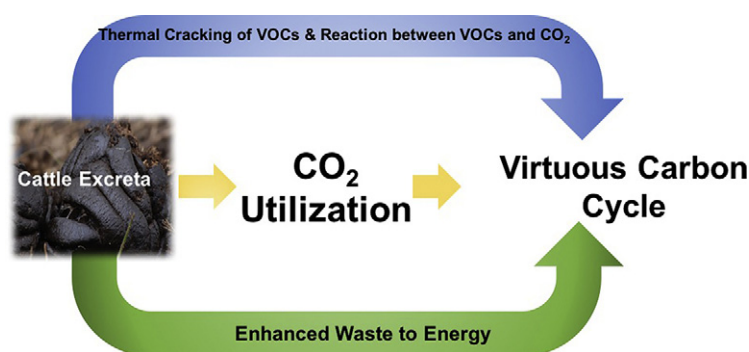
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### HIGHLIGHTS

- Use of animal manure as an energy source
- No additional energy input for mitigating pyrolytic oil
- Enhanced generation of pyrolytic gases in the thermal degradation of cattle excreta

### GRAPHICAL ABSTRACT



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### ABSTRACT

To develop the environmentally benign thermo-chemical process, this study placed great emphasis on the influence of CO<sub>2</sub> on pyrolysis of cattle excreta for energy recovery. To this end, this study evaluates the possible enhanced energy recovery from cattle excreta using CO<sub>2</sub> as reaction medium/feedstock in the thermal degradation of cattle excreta. The enhanced generation of CO in the presence of CO<sub>2</sub> reached up to 15.15 mol% (reference value: 0.369 mol%) at 690 °C, which was equivalent to ~4000 times more generation of CO. In addition to the enhanced generation of CO, the enhanced generation of H<sub>2</sub> and CH<sub>4</sub> in the thermal degradation of cattle excreta in CO<sub>2</sub>. Thus, the findings of this study revealed two genuine roles of CO<sub>2</sub>: 1) enhanced thermal cracking of volatile organic carbons (VOCs) evolved from the thermal degradation of cattle excreta and 2) direct reaction between VOCs and CO<sub>2</sub> via gas phase reaction.

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### 1. Introduction

The global demand for meat and dairy products in accordance with our economic prosperities has increased continuously and

rapidly (Bruinsma, 2003). Livestock is housed in closed quarters inside animal feeding operations or on outside feedlots in the industrial model for the massive livestock production (Starmer, 2007). The average daily production of cattle excreta is over 60 kg per cow in a dairy farm (Nennich et al., 2005). This situation has evoked a great deal of concerns to dispose of livestock manure without environmental burdens (Vukina, 2003). Thus, manure management

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has been regarded as a critical environmental issue (Ilea, 2009). While many agricultural practices use manure as a fertilizer, the amount of nutrients such as P and N applied to arable land from livestock manure has begun to exceed the requirements of crop growth and lead to water contamination due to surface runoff (Schoumans et al., 2010). Therefore, it is highly desirable to develop a new class of livestock manure managements.

In many developing countries, dried cow excreta are being used as a fuel through an uncontrolled oxidation condition (i.e., incomplete combustion). Consequently, the uncontrolled oxidation inevitably leads to the generation of particulate matters and unburned hydrocarbons, thereby resulting in significant air pollution and environmental threat (Mudway et al., 2005). Meanwhile, in many developed countries, cow manure has been used to produce biogas via anaerobic digestion (Cavinato et al., 2017; Díaz et al., 2016), but energy density of biogas is substantially lower than that of natural gas due to the high content of CO<sub>2</sub> (e.g., ~50%) in biogas. Also, many biogas plants often do not have proper containment facilities to prevent discharge of untreated manures into the environment (Chadwick et al., 2015). Even though it is necessary to develop an improved cattle excreta treatment technology while recovering energy, our concerns associated with proper livestock manure disposal have been limited to the mitigation of odor, air pollution controls, surface and ground water pollution, and antibiotic resistance (Graham and Nachman, 2010; Song et al., 2017). Animal manure has been considered as renewable carbon source due to its biomass-derived origin (i.e., carbon neutrality) (Klass, 1998; Vazić et al., 2015). This can be a catalyst to explore a viable means for exploiting livestock excreta as substrate for biofuels.

In these regards, the thermo-chemical processes such as pyrolysis and gasification has been considered as one of the promising fuel processing technologies from the renewable carbonaceous feedstocks (Bartholomew and Farrauto, 2006; McKendry, 2002a; McKendry, 2002b). Pyrolysis (i.e., thermo-chemical process for the decomposition of organic feedstocks in the absence of oxygen and water) and gasification (i.e., thermo-chemical process for the conversion of carbonaceous feedstocks into light gases such as H<sub>2</sub>, CO, and CO<sub>2</sub> in the presence of oxygen and water) results in the thermal degradation of carbonaceous feedstock to produce a blend of gaseous (light molecular weight gases such as H<sub>2</sub> and CO), liquid (heavy molecular weight compounds obtained after proper condensation), and solid products (chars) (Huber et al., 2006). For instance, slow pyrolysis mainly generates solid chars whereas fast pyrolysis produces liquid fuels (i.e., bio-oil) (Authier et al., 2009; Garcia-Perez et al., 2008; Lee et al., 2013; Williams and Besler, 1996). Moreover, the products of the thermo-chemical processes are highly compatible with the current industrial infrastructures (Verma et al., 2012). Compared to direct combustion of solid fuels (e.g., cattle excreta), energy recovery via the thermo-chemical process requires much less oxygen (or no oxygen) and generate less pollutants such as unburned hydrocarbons and nitrous oxides (Kumar et al., 2009).

Nevertheless, one of demerits of the thermo-chemical processes is energy-intensive. Thus, the increase in the thermal efficiency of gasification should be achieved via coupling with pyrolysis. For instance, the enhanced thermal efficiency can be directly applicable in gasification since pyrolysis is an intermediate step for gasification (Higman and Burgt, 2003). Hence, the scope of this study is intentionally limited to pyrolysis of cattle excreta to avoid any complexities. Previous literatures reported the generation of CO from various organic feedstocks can be enhanced by CO<sub>2</sub> (Lee et al., 2017a; Lee et al., 2017b; Lee et al., 2017c). However, there have hardly been studies about thermally decomposition of real animal manure such as cattle excreta under CO<sub>2</sub>. Thus, the main purpose of this study is to investigate the effects of CO<sub>2</sub> on pyrolysis of cattle excreta as a strategy of both managing agricultural organic wastes and utilizing CO<sub>2</sub> as reaction medium and feedstock in the energy recovery process. To this end, this study reported 1) the characterization of thermal degradation of cattle excreta in N<sub>2</sub> and CO<sub>2</sub>, 2) the analysis of pyrogenic gaseous products from pyrolysis of cattle excreta

in N<sub>2</sub> and CO<sub>2</sub>, 3) the comparison of benzene derivatives from pyrolysis of cattle excreta in N<sub>2</sub> and CO<sub>2</sub>.

## 2. Materials and methods

### 2.1. Materials

Cattle excreta was collected from National Institute of Animal Science (NIAS) in Korea. The gases (N<sub>2</sub> and CO<sub>2</sub>) used for the experimental work were ultra-high purity. Dichloromethane (>99.9%) used to tap high molecular hydrocarbons was purchased from Sigma-Aldrich. Cellulose and lignin for estimating heat of combustion were also purchased from Sigma-Aldrich. An IKA oxygen bomb calorimeter was used to measure the heat of combustion.

### 2.2. Thermogravimetric analysis of cattle excreta

Thermogravimetric analysis (TGA) of cattle excreta under N<sub>2</sub> and CO<sub>2</sub> atmospheres was conducted in triplicates using a Mettler Toledo TGA/DSC unit. The TGA tests are conducted at a heating rate of 10 °C min<sup>-1</sup> from 25 to 900 °C. A 10 ± 0.1 mg of cattle excreta was used for an analysis. The total flow rate of purge and protective gas in the TGA test 100 mL min<sup>-1</sup>.

### 2.3. Pyrolysis setup

A quartz tube (OD: 25 mm, ID: 22 mm, L: 0.6 m) was used as a tubular pyrolysis reactor. A 1.2 ± 0.1 g of cattle excreta was loaded on an alumina boat and the boat was located on the center of the reactor (i.e., batch-type loading of feedstock). Total gas flow rate was controlled to 600 mL min<sup>-1</sup> by Brooks Instrument 5850E mass flow controllers (MFCs). Temperature inside the reactor was measured using a thermocouple and controlled by a temperature-programmable tubular furnace. Tar was collected by a condenser hooked up with a chiller (4 °C). Pyrolytic gases were quantified by means of a micro GC (Inficon 3000A). Calibration data and QA/QC of the micro GC is in supporting information. The collected tar was analyzed by a GC/TOF-MS (Agilent 7890B/ALMSCO) system. The GC/TOF-MS analysis conditions are in supporting information.

## 3. Results and discussion

### 3.1. Characterization of thermal degradation of cattle excreta in N<sub>2</sub> and CO<sub>2</sub>

The thermogravimetric analysis (TGA) tests were performed at a heating rate of 10 °C min<sup>-1</sup> from 25 to 900 °C to characterize the thermal degradation of cattle excreta in N<sub>2</sub> and CO<sub>2</sub>. The representative mass decay curves (thermogram) in N<sub>2</sub> and CO<sub>2</sub> are shown in Fig. 1. To effectively differentiate the influence of CO<sub>2</sub> in pyrolysis of cattle excreta, the thermal degradation rates (differential thermogram: DTG) and differential scanning calorimeter (DSC) curves were also incorporated in Fig. 1a and b, respectively.

As evidenced in Fig. 1, mass decay of cattle excreta in N<sub>2</sub> and CO<sub>2</sub> is nearly identical at temperatures lower than 800 °C. Thus, there is nearly negligible influence of CO<sub>2</sub> associated with any physical aspects such as onset and end temperature of the thermal degradation. This phenomenon is well described in both DTG and DSC curves as the different thermal degradation mechanisms induced by CO<sub>2</sub> results in the different thermal degradation rates as well as heat transfer (heat flux) toward the sample loaded in the TGA unit. This observation signifies that the additional energy for employing CO<sub>2</sub> is not necessary during the thermal degradation of cattle excreta. Furthermore, Fig. 1 indirectly suggests that the heterogeneous reaction between the sample surface and CO<sub>2</sub> should be excluded because otherwise the heterogeneous reaction induced by CO<sub>2</sub> results in the different thermal degradation behaviors

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