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Strategic use of CO_2 for co-pyrolysis of swine manure and coal for energy recovery and waste disposal

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ABSTRACT

Here in this study, the genuine role of CO_2 in co-pyrolysis of swine manure and coal was mainly investigated to increase the thermal efficiency of the thermo-chemical process. The TGA test of swine manure and coal revealed that the CO_2 co-feeding impact on any reactions ($\leq$740 °C) between CO_2 and the sample surface (*i.e.,* heterogeneous reaction) should be excluded. A batch-type co-pyrolysis revealed two genuine CO_2 co-feeding impacts on co-pyrolysis of swine manure and coal. First, CO_2 can be an additional source for C and O through a plausible reaction between pyrolytic oil and CO_2, which led to the enhanced generation of CO by the conversion of volatile organic carbons (VOCs) evolved from thermal deconstruction of pyrolytic substrate. Second, CO_2 expedite the thermal cracking of VOCs, which also resulted in the more generation of H_2 and CH_4. Two genuine roles of CO_2 in co-pyrolysis of swine manure and coal occurred independently. All experimental findings will be directly applicable to the gasification process since pyrolysis is an intermediate step for the gasification.

1. Introduction

South Korea produces annually about more than one million metric tons of pork, positioning at 11th in the world [1]. According to OECD, Korea's per capita meat consumption (*i.e.,* annual basis) breaks down 24.3 kg of pork, 15.4 kg of chicken, and 11.6 kg of beef with its total larger than China and Japan by 4 to 16 kg. To satisfy this high demand for pork, livestock production has heavily relied on concentrated animal feeding operations (CAFOs) in Korea. Albeit efficient in pork production, CAFOs inevitably produce large quantity of swine manure, which far exceeds the capacity of land to assimilate the organic carbon and nutrient manures [2–7]. The livestock production resulted in 47 million tons of grand total manure production including swine manure of 18.4 million tons (40%) in Korea [8]. Despite debate in the interdisciplinary areas between agricultural and environmental sector, it is very desirable to establish a cost-effective and ecofriendly platform for the dispose of swine manure [6,9–11].

In this context, harnessing swine manure as a biomass resource for energy production (*i.e.*, bioenergy) can be sustainable disposal route with financial benefits [11]. Bioenergy from swine manure also accounts for a substantial part of energy demand because of avoiding the problems associated with dedicated bioenergy crops [12]. In many developing countries, dried livestock manures are being used as a fuel through an uncontrolled oxidation condition (*i.e.,* combustion). Consequently, uncontrolled oxidation inevitably leads to the generation of highly active particulate matters and unburned hydrocarbons (UHCs), thereby resulting in air pollution and posing a potential environmental threat [13]. Meanwhile, in many developed countries, livestock manure has been used to produce biogas via anaerobic digestion (AD) [14–17], but energy density of biogas is substantially lower than one of natural gas owing to a high content of CO_2 (~50%) in biogas. In addition to the low content of CH_4 in biogas, the inevitable carbon deposit into microbes cannot be avoided, albeit efficient in the volume reduction of manure. Subsequently, this poses another disposal problems [18].

In these regards, among the various ways of using bioenergy [14–17,19–24], thermo-chemical processes like pyrolysis and gasification are thought as a promising fuel processing technology since carbonaceous feedstock can be completely converted into combustible gas and oil [25–31]. Nevertheless, their practical implementations have been very limited since the thermo-chemical processes are suitable for mass production. Heterogeneous compositional matrix of manure has been also regarded as one of obstacles for exploiting manure as a raw

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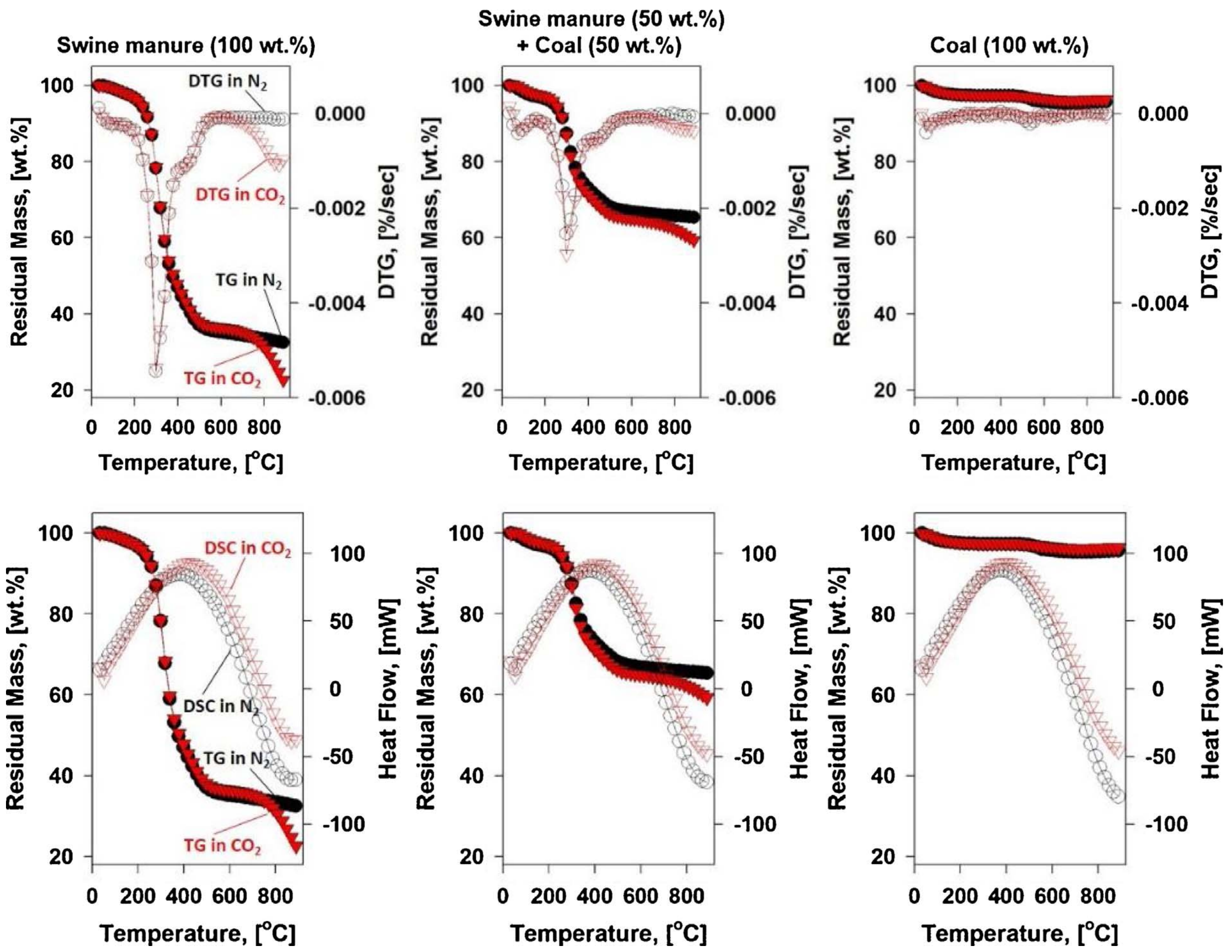

Fig. 1. Representative mass decay curves, differential thermogram (DTG), and differential scanning calorimeter (DSC) from the TGA tests of swine manure, coal, and the equivalent mass ratio of swine manure and coal from 25 to 900 °C (10 °C min^{-1}) in N_2 and CO_2.

material for the thermo-chemical processes. Thus, the use of manure blended with coal provides a great venue for resolving the disposal problem associated with manure while eco-friendly extracting energy. However, one of demerits of pyrolysis and gasification is energy-intensive. In this context, an increase in thermal efficiency of pyrolysis and gasification should be developed.

Thus, this study laid a great emphasis on the mechanistic understanding of CO_2 in co-pyrolysis of swine manure and coal to increase the thermal efficiency and sustainability of pyrolysis. The research scope of this study intentionally limited to co-pyrolysis of swine manure and coal since pyrolysis is an intermediate step for the gasification process. In other words, all experimental findings describing the pyrolytic characteristics has a great importance for syngas yield and performance promotion for the gasification process [25–27,29,30]. A great deal of researches covering pyrolysis and gasification of individual component has been conducted. To date, not much research experimental work associated with co-pyrolysis of coal and swine manure has been compiled. Furthermore, to our best knowledges, co-pyrolysis of coal and swine manure in CO_2 has not been investigated even though the addition of swine manure to coal during the thermal degradation may have various effects. Thus, first of all, the thermal degradation of swine manure and coal in N_2 and CO_2 was characterized thermo-gravimetrically. Second, the pyrogenic products generated from co-pyrolysis of swine manure and coal in N_2 and CO_2 were characterized to chase the mechanistic role of CO_2. Third, the susceptibility of CO_2 in co-pyrolysis of swine manure and coal was discussed.

2. Materials and methods

2.1. Materials

Swine manure was obtained from National Institute of Animal Science (NIAS) in Korea. Sub-bituminous coal was obtained from Korea Institute of geoscience and mineral resources and it was collected from Kangwon Province in Korea. Prior to the experimental work, swine manure was dried using a dry oven at 80 °C for 3 days. Based on the ultimate analysis of swine manure (*i.e.,* dry basis), swine manure contains carbon (43.66 wt.%), hydrogen (4.18 wt.%), nitrogen (2.47 wt.%), sulphur (0.48 wt.%), and oxygen (33.51 wt.%). The proximate analysis of swine manure (*i.e.*, dry basis) shows that swine manure contains ash (15.20 wt.%), volatile matter (62.90 wt.%), and fixed carbon (21.90 wt.%). Both swine and coal were pulverized using a Thomas Wiley Mill (USA) and their average size are less than 0.5 mm. The ultra-high purity gases (N_2 and CO_2) were used for the experimental work. Dichloromethane (≥ 99.9%) used to tap high molecular hydrocarbons was purchased from Sigma-Aldrich.

2.2. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) of swine manure and coal in N_2 and CO_2 was conducted in triplicates using a Mettler Toledo TGA/DSC unit (Switzerland). The sample was heated from 25 to 900 °C with 10 °C min^{-1}. A 10 ± 0.1 mg of sample was used for each TGA test. The total flow rate of purge and protective gas in the TGS test were 100 mL min^{-1}.

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