Energy 153 (2018) 726–731

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Effects of calcium carbonate on pyrolysis of sewage sludge

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ARTICLE INFO

Article history:
Received 25 October 2017
Received in revised form
21 February 2018
Accepted 17 April 2018
Available online 18 April 2018

Keywords:
Sewage sludge
$CaCO_3$
Pyrolysis
Waste-to-energy
Thermal treatment

ABSTRACT

This study demonstrates that calcium carbonate ($CaCO_3$) allows not only enhancement of the production of CO as syngas, but also reduction of the content of polycyclic aromatic hydrocarbons (PAHs) in the pyrolytic products from sewage sludge. CO_2 was formed by the decomposition of $CaCO_3$ in pyrolysis. The CO_2 derived from $CaCO_3$ enhanced thermal cracking of volatile organic carbons (VOCs) generated during the pyrolysis of sewage sludge and provided an additional source of C and O, likely enhancing the production of CO at >650 °C. In addition, more solid product was converted into gaseous and liquid products by the addition of $CaCO_3$ in the pyrolysis of sewage sludge. This work suggests that $CaCO_3$ can be used as an inexpensive source of CO_2 that increases thermal efficiency of the pyrolysis process and reduces the evolution of harmful chemical species such as PAHs during thermal treatment of the byproduct during processing at municipal and industrial wastewater treatment facilities (*i.e.*, sewage sludge).

1. Introduction

Sewage sludge is an unavoidable byproduct in wastewater treatment plants [1]. The increase in the population in cities and urbanization have led to increasing the generation of sewage sludge, thereby resulting in the treatment of sewage sludge has become a matter of great concern [2]. It was estimated that the annual production of sewage sludge in the US will be 10 million Tds (tons dry solids) in 2020 [3]. In Korea, about 3 million tons of sewage sludge were generated in 2008 [4].

Landfilling is a common disposal process for sewage sludge. Nevertheless, disposal of sewage sludge in landfills is not desirable due to the limited available landfill volume [5]. Sewage sludge has also been used as farmland fertilizer with proper activation such as sulfuric acid activation [6] and modification of pore structure [7]. However, this use is limited due to potential contamination of the land by organic contaminants [8] and pathogenic bacteria [9] existing in sewage sludge. Even though incineration of sewage sludge can effectively recover energy [10,11], the process requires rigid control of generation of volatile pollutants such as heavy metals (*e.g.*, Cd, Pb, Cu) [12], dioxins [13], and acidic species [14].

Pyrolysis, a thermal decomposition processing of carbonaceous materials under oxygen and water-free circumstances, is less sensitive to impurities in feedstocks and emits less air pollutants than combustion [15]. Furthermore, all pyrolytic products (*i.e.*, syngas, pyrolytic oil, and char) are highly compatible with existing industrial infrastructures [16]. Despite these advantages, pyrolysis is energy-intensive; thus, it is truly essential to develop a less energy-intensive pyrolysis process for treating wastes such as sewage sludge.

Even though considerable work has been documented with respect to pyrolysis (mainly for biochar applications) [17,18], limited studies reported that alkaline mineral matter affects the rate of thermochemical processes of organic substances [19–21]. For instance, interactions between potassium (K) content and temperature and CO_2 partial pressure were studied [19]. It was reported that an increased gasification rate by magnesium (Mg) is proportional to the amount of Mg in the feedstock [20]. Potassium carbonate (K_2CO_3) and calcium hydroxide ($Ca(OH)_2$) affect compositions of pyrolytic products from woody biomass [21]. However,

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https://doi.org/10.1016/j.energy.2018.04.100
0360-5442/

Table 1
Proximate analysis of sewage sludge.

Moisture (wt.%)	6.16 (±0.05)
Volatiles (wt.%)	54.36 (±0.03)
Fixed carbon (wt.%)	1.99 (±0.06)
Ash (wt.%)	37.49 (±0.03)

the role of such mineral compounds in pyrolysis of organic waste (*e.g.*, sewage sludge) has not been fully investigated yet. In these respects, pyrolysis of sewage sludge has been performed with calcium carbonate ($CaCO_3$) to explore how the mineral affects pyrolysis of sewage sludge and to understand the role of $CaCO_3$ in the sewage sludge pyrolysis. This study proposes a potential treatment of sewage sludge achieving enhanced energy recovery from such inevitable municipal waste.

2. Materials and methods

2.1. Materials

Sewage sludge was collected from a water resource recovery facility in Seoul, Republic of Korea. The sludge was dewatered by a high-solids centrifuge prior to experiments. Proximate analysis of the dried sludge was performed as described elsewhere [22], as shown in Table 1. $CaCO_3$ (≥99%) was purchased from Sigma-Aldrich. Two mixtures of $CaCO_3$ and sewage sludge were prepared: 9 wt.% $CaCO_3$ and 33 wt.% $CaCO_3$. Ultra-high purity nitrogen (N_2) gas was used for thermogravimetric analysis (TGA) and pyrolysis of the samples, purchased from Green Gas, Korea.

2.2. TGA experiments

TGA experiments of $CaCO_3$, sewage sludge, and $CaCO_3$/sewage sludge mixtures were conducted from 25 to 900 °C (10 °C min^{-1}) using a Mettler Toledo STAR[e] TGA instrument. The N_2 flow rate was 60 mL min^{-1} (20 mL min^{-1} of protective gas and 40 mL min^{-1} of reactive gas). The amount of sample loaded for an experiment was 12 ± 0.2 mg.

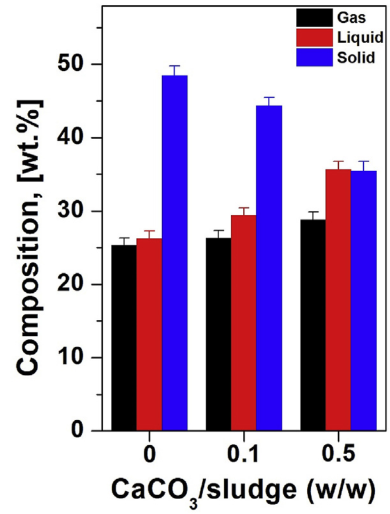

Fig. 2. Effects of $CaCO_3$ loading on the composition of gaseous, liquid, and solid products derived from sewage sludge pyrolysis. Mean values of replicates ($n = 3$) are reported with standard deviations given as error bars.

2.3. Pyrolysis experiments

A quartz tube that had an outer diameter (OD) of 25 mm, an inner diameter (ID) of 22 mm, and a length (L) of 0.6 m was used as a pyrolysis reactor for the samples. For an experiment, a 3.6 ± 0.5 g of each sample was loaded inside the reactor located in the center of the reactor. Pyrolysis was performed in flowing N_2 (600 mL min^{-1}). Mass flow controllers (MFCs) (Brooks Instrument) controlled the gas flow rate. The reactor was heated (10 °C min^{-1}) in a temperature-programmable tubular furnace (DAIHAN Scientific).

2.4. Chemical analysis

For *in-situ* analysis of gases in the effluent from the pyrolysis, an INFICON 3000A micro gas chromatograph (GC) with a thermal conductivity detector (TCD) was used. The micro GC was calibrated using a standard gas mixture (RIGAS). The chemical compounds in

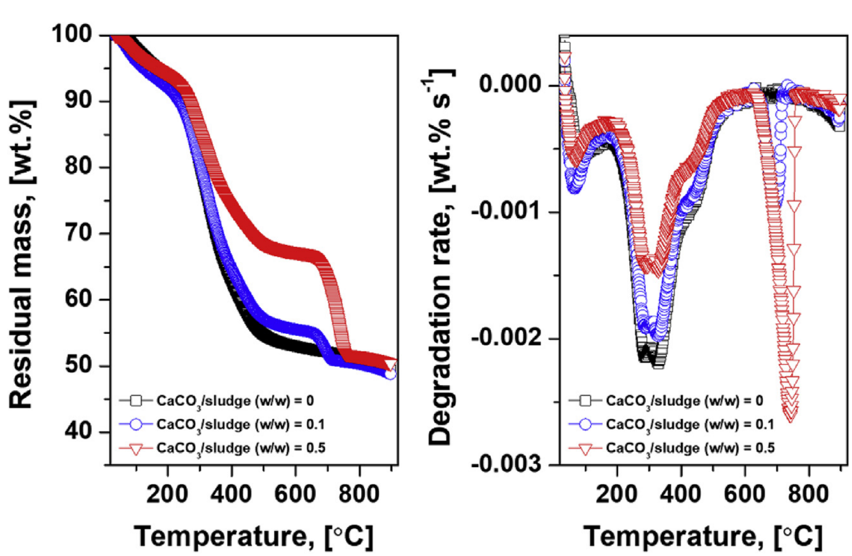

Fig. 1. Thermograms (TGs) and differential thermograms (DTGs) for thermal degradation of sewage sludge with $CaCO_3$ according to the different weight ratio of $CaCO_3$ to sewage sludge. Mean values of replicates ($n = 3$) are reported and standard deviations of the mean values are around 2%.