



# Carbon dioxide assisted sustainability enhancement of pyrolysis of waste biomass: A case study with spent coffee ground



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## HIGHLIGHTS

- Enhanced generation of carbon monoxide (CO) via using CO<sub>2</sub> as reaction medium.
- Expediting the thermal cracking of volatile organic compounds (VOCs) induced by CO<sub>2</sub>.
- In situ reduction of tar under the presence of CO<sub>2</sub>.
- Morphological modification of biochar under the presence of CO<sub>2</sub>.

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## ABSTRACT

This work mainly presents the influence of CO<sub>2</sub> as a reaction medium in the thermo-chemical process (pyrolysis) of waste biomass. Our experimental work mechanistically validated two key roles of CO<sub>2</sub> in pyrolysis of biomass. For example, CO<sub>2</sub> expedited the thermal cracking of volatile organic compounds (VOCs) evolved from the thermal degradation of spent coffee ground (SCG) and reacted with VOCs. This enhanced thermal cracking behavior and reaction triggered by CO<sub>2</sub> directly led to the enhanced generation of CO (~3000%) in the presence of CO<sub>2</sub>. As a result, this identified influence of CO<sub>2</sub> also directly led to the substantial decrease (~40–60%) of the condensable hydrocarbons (tar). Finally, the morphologic change of biochar was distinctive in the presence of CO<sub>2</sub>. Therefore, a series of the adsorption experiments with dye were conducted to preliminary explore the physico-chemical properties of biochar induced by CO<sub>2</sub>.

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## 1. Introduction

The global environmental issue triggered by anthropogenic greenhouse gases (GHGs) has gained public acceptance due to its potential environmental and economic threat, which has been justified by our longstanding scientific research (Girod et al., 2009; Li et al., 2015; Sperow, 2014). Among numerous anthropogenic GHGs, CO<sub>2</sub> has drawn public attention due to its tremendous generation from harnessing fossil fuels (Chen et al., 2015; Sperow, 2014). Thus, our environmental awareness has simultaneously triggered most scientific and engineering researches associated with carbon capture and storage (CCS) and renewable energies, which partially alleviate environmental threats. In parallel, the concept of carbon neutrality has been emphasized since our communities' endless demand for carbon would be indispensable

(Bluhm et al., 2012; Chen et al., 2015; Sanchez et al., 2015; Serrano-Ruiz and Dumesic, 2011). Among various categories of biorefinery, biofuels (*i.e.*, bio-alcohol, biodiesel, biohydrogen, and so on) have been recognized as an initial step for biorefinery (Koutinas et al., 2014; Maity, 2015a,b). Thus, the first generation of biofuels based on edible crops has been commercially produced (Maity, 2015b) and their use has been politically supported and recommended by means of renewable portfolio standard (RPS) and renewable fuel standard (RFS) (Abdmouleh et al., 2015; Girod et al., 2009; Kwon et al., 2013a,c, 2014a,b; Luque et al., 2008).

Although numerous advantages of biofuels have been well recognized, the concrete and optimized production of biofuels on the basis of inedible crops and biomass (*i.e.*, 2nd and 3rd generation of biofuels) has not been fully established (Aikawa et al., 2013; de Souza et al., 2014; Guo et al., 2014; Korzen et al., 2015; Wang et al., 2014). Furthermore, seasonal and regional variations associated with the supply chain of biomass as an energy feedstock are still problematic (Kwon et al., 2013b; Williams and Laurens, 2010). In order to resolve and/or abate the problems stated above,

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the concept of waste-to-energy (WtE) via the thermo-chemical pathway has been proposed as one of the feasible alternatives since the thermo-chemical process (pyrolysis and gasification) is suitable for mass production and for compatibility with the current infrastructures of the energy and chemical industry (Amponsah et al., 2014; Chen et al., 2015; Chuetor et al., 2015; Maity, 2015a; Williams and Laurens, 2010). Thus, preferably, we need to explore innovative ways to enhance the thermal efficiency of the current thermo-chemical process. More preferably, developing new engineering applications via reuse of CO<sub>2</sub> as a reaction medium and raw material for the thermo-chemical process would be the best scenario because we can possibly achieve a virtuous cycle, which would lead to the strong viability of biofuels (Kaufman et al., 2008; Kwon et al., 2012a, 2013c). Furthermore, our previous work reported that the significant amount of tar could be reduced via using CO<sub>2</sub> as reaction medium (Kwon et al., 2012b). Unfortunately, the influence of CO<sub>2</sub> in the thermo-chemical process has not been fully developed.

Thus, this work mainly investigated the pyrolysis process because pyrolysis has been known as the intermediate step for gasification (Kwon et al., 2012b); our mechanistic understanding of CO<sub>2</sub> in the pyrolysis process would be a guideline for the utilization of CO<sub>2</sub> in the gasification process. Thus, this work is limited to the influence of CO<sub>2</sub> in the pyrolysis process. In order to validate the concept of WtE, the goal of this research is to study in depth the pyrolysis of SCG as a case study. The numerous literatures associated with the thermo-chemical process of the conventional fuel such as coal have been well archived, but the pyrolysis process of waste biomass has not been fully developed (Jayaraman and Gokalp, 2015; Maity, 2015b; Marchand et al., 2015; Wu et al., 2015). Furthermore, the influence of CO<sub>2</sub> in pyrolysis of waste materials has not been fully archived. Thus, this study will fundamentally investigate the influence of CO<sub>2</sub> in the pyrolysis process to achieve the enhanced thermal efficiency of gasification. Lastly, a series of adsorption tests with biochar obtained from N<sub>2</sub> and CO<sub>2</sub> was conducted with dye (*i.e.*, methylene blue: MB) to preliminarily explore the influence of CO<sub>2</sub> on biochar.

## 2. Methods

### 2.1. Sample preparation and chemical reagents

Spent coffee ground (SCG) used in this work was obtained from a local coffee shop in Seoul, Korea. The grounds were dried at 90 °C for 72 h, and the moisture content was measured at less than 1%. The dried samples were then stored at room temperature in a sealed container. All gases (N<sub>2</sub> and CO<sub>2</sub>) used for the experiments were ultra-high purity (UHP) and purchased through Daesung (Seoul, Korea).

### 2.2. Thermo-gravimetric analysis (TGA)

Experiments were carried out in N<sub>2</sub> and CO<sub>2</sub> using a Netzsch STA 449 F1 Jupiter® TGA unit. A series of TGA tests were carried out at a heating rate of 10 °C min<sup>-1</sup> over a temperature range of ambient temperature to 900 °C. The flow rate of the purge and protective gas was a total 150 mL min<sup>-1</sup> and ~10 mg of sample was loaded into the TGA unit.

### 2.3. Tubular reactor (TR) setup

A tubular reactor (TR), made of 1 inch outer diameter (OD) quartz tubing (Chemglass CGQ-0900T-13) and 1 inch Stainless Ultra Torr Vacuum Fitting (Swagelok SS-4-UT-6-400), was used. In addition, the length of the TR unit was 0.6 m. The sample of

SCG (10 g) was loaded into the reactor. The required experimental temperatures were achieved using a split-hinged furnace (AsOne, Japan). The temperature was simultaneously monitored by an S-type thermocouple to ensure the experimental temperature was met. An insulation collar (high temperature Duraboard insulation) at the end of the furnace was used to block heat transfer (*i.e.*, heat loss) during operation and protect the quartz tubing. All gas flow rates (500 mL min<sup>-1</sup>) were set using a Brooks mass flow controller (5850 series E). A computer-aided control system by LabVIEW (National Instrument, USA) was employed. The condensable pyrolytic products were collected with a condenser, and the temperature of the condenser was maintained at 4 °C with a chiller.

### 2.4. Pyrolytic gas measurement

The effluent of the TGA was sent to a GC/MS (Agilent 9890/4973) or micro-GC (Agilent 3000A) for identification and quantification of the chemical species from the TGA unit. The lag time of the sample from the TGA unit to the injection block, located on the GC/MS, was calculated to be less than 1 s, based on a 3 mL volume transfer line (Netzsch Unit). The sampling system was maintained at greater than 300 °C to mitigate condensation and/or adsorption of chemical species onto the system surface.

The GC was equipped with a capillary column (0.25 mm × 30 m HP-5MS), which was directly interfaced to a quadrupole mass spectrometer. Identification of the species was accomplished by matching the gas chromatographic retention times to those of the pure components and the mass spectral fragmentation patterns to species found in standard MS libraries. Permanent gases (*i.e.*, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>) and C<sub>1</sub> and C<sub>2</sub> chemical species were determined using a Carboxen-1010 (Supelco #25467) connected to the TCD. In addition, to obtain C<sub>4</sub> species, a micro-GC (Agilent 3000) was used.

### 2.5. Characterization of biochar and adsorption experiments

The surface morphologies of biochar obtained from N<sub>2</sub> and CO<sub>2</sub> experimental conditions were preliminarily characterized by scanning electron microscopy (SEM). A series of batch type adsorption tests was conducted in 25 mL glass vials (Fisher Scientific, USA) at 25 ± 1 °C. Adsorption isotherm were measured by adding 0.1 g biochar from N<sub>2</sub> and CO<sub>2</sub> into 20 mL methylene blue (MB) solution ranging from 9.9 to 136.6 mg L<sup>-1</sup> at pH 7 and then the suspensions were agitated at 150 rpm for 24 h. The adsorption capacity values at equilibrium ( $q_e$ ) were determined by  $q_e(\text{mg g}^{-1}) = \frac{(C_0 - C_e)V}{W}$ , where C<sub>0</sub> and C<sub>e</sub> are initial and equilibrium concentrations of adsorbate (mg L<sup>-1</sup>), respectively; W is the dry mass of the adsorbent (g) and V is the volume of the solution (L). Any filters were not used for the separation of solid and liquid in order to avoid possibility of partly removing MB in solution with syringe- or membrane filter. The supernatants were collected via centrifugation and then used for measurement of MB concentration in bottles. The concentrations of MB in the solutions were measured with a UV-vis spectrophotometer (Hach DR/4000, USA) at wavelength 665 nm.

## 3. Results & discussion

### 3.1. Characterization of the thermal decomposition of spent coffee ground (SCG) in CO<sub>2</sub>

A series of thermo-gravimetric analysis (TGA) tests at the heating rate of 10 °C min<sup>-1</sup> from 25 °C to 900 °C were with the SCG sample to characterize and to compare the thermal degradation of SCG in N<sub>2</sub> and CO<sub>2</sub>. In addition, the thermal degradation rate was depicted with the differential thermogram (DTG) to clearly

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