



Carbon dioxide assisted co-pyrolysis of coal and ligno-cellulosic biomass



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ABSTRACT

This work mechanistically investigated the influence of CO₂ in co-pyrolysis of sub-bituminous coal and main constituents of ligno-cellulosic biomass (cellulose and hemicellulose). Our experimental work identified the crucial role of CO₂ in co-pyrolysis of coal and biomass. For example, CO₂ not only enhanced the thermal cracking behavior of VOCs evolved from the thermal degradation of a carbonaceous solid sample (*i.e.*, sub-bituminous coal, cellulose, and xylan) via blocking the addition reaction, but also directly reacted with VOCs and CO₂. The genuine effects induced by CO₂ led to a significant reduction of condensable hydrocarbons (*i.e.*, tar), which directly lead to a significant enhancement of syngas production and modification of ratio of CO to H₂: the ratio of CO to H₂ was increased approximately ~1200% at 680 °C in pyrolysis of coal in the CO₂ environment and the ratio of CO to H₂ was adjustable by means of using a different amount of CO₂ during the pyrolysis process of carbonaceous samples. Furthermore, the identified role of CO₂ would be applicable to the in-situ air pollution control in various industrial applications, such as steelworks. Lastly, the identified role of CO₂ in pyrolysis will be applied in the gasification process since pyrolysis is the intermediate step for the gasification process.

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1. Introduction

Based on the annual report of the U.S. Department of Energy (DOE), the world energy consumption and/or production in 2010 was estimated as $\sim 5 \times 10^{20}$ J. The identified total reservoir of fossil fuels was estimated to be ~ 800 times greater than current energy consumption. Considering methane hydrate as a feasible energy source in the future, all remaining fossil fuels were estimated as ~ 4000 times greater than current energy consumption. Unfortunately, utilizing these fossil fuels is not possible due to economic, technical, and environmental barriers [1–3]. Furthermore, the uneven geological distribution of fossil fuels has triggered the energy security issue that has become one of top priorities in developed countries [4–6].

Besides this energy security issue, a great deal of researches covering our social, scientific, and engineering aspects has confirmed the global environmental issues, such as climate change (*i.e.*, global warming), thus, the detrimental environmental impacts from the global environmental issues have gained the public acceptance [7–10]. Various anthropogenic greenhouse gases

(GHGs) have been identified as the main contributors accelerating the global environmental issues [11–13]. Among GHGs, carbon dioxide has been identified the major contributor triggering the climate change since the current energy infrastructure was based on fossil fuels (*i.e.*, petro-derived oil) [8]. Thus, unprecedented scientific and engineering efforts have been initiated to resolve and to alleviate the global environmental impacts via developing the cutting-edged technologies, such as various carbon free renewable energies [14–20] (*i.e.*, wind power, photovoltaic (PV), geothermal, *etc.*) and carbon capture and storage (CCS) [7,9,21]. The concept of carbon neutrality, meanwhile, has been highlighted since our dependence on carbon in chemicals, commodities, and fuels was inevitable [19,22–24]. Thus, the concept of bio-refinery has been initiated and the commercialized production of the 1st generation of biofuels (*i.e.*, biodiesel and bioethanol from edible crop) has been accomplished [22,25]. Moreover, the expansion of biofuels has been strongly encouraged by political enactment and/or reinforcement, such as the renewable fuel standard (RFS) [15,26,27].

However, the first generation of biofuels brought forth unexpected side effects including an ethical dilemma and the soaring price of crops [28,29]. Thus, the concept of 2nd and 3rd generation of biofuels was proposed, but the technical barriers for the commercialized production of them were still challenging. Compared to conventional fossil fuels, harnessing biomass as an initial

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feedstock for energy has been known to be being extremely difficult due to its well-known heterogeneous matrix and the evolutionary functionalized structures of biomass [18,19,22,30,31]. Moreover, the seasonal variation of biomass would be problematic for the use of biomass as an initial feedstock for energy [32,33]. In addition, the total quantity of possibly collected biomass to sustain current energy consumption would be insufficient compared to coal [34–36]. Thus, it would be desirable to find a universal fuel processing technology compatible with biomass and conventional carbonaceous fuel such as coal [33,37].

The thermo-chemical process known as pyrolysis and gasification has been recognized as a promising fuel processing technique since most carbonaceous solids can be universally treated and are suitable for mass production [38,39]. One of main drawbacks of the thermo-chemical process is that it is an energy-intensive process [33]. Thus, developing new technical advances to enhance thermal efficiency should be implemented. Preferably, the enhanced sustainability via applying CO₂ as a reaction medium and chemical feedstock in the thermo-chemical process would be environmentally benign and has the potential to evolve into our ultimate goal associated with carbon management. In order to achieve this, this work will investigate the influence of CO₂ in co-pyrolysis of coal and ligno-cellulosic biomass. The scope of this work was intentionally limited to the co-pyrolysis of coal and ligno-cellulosic biomass since pyrolysis is known as an intermediate step in the gasification process. For example, the experimental findings of this work are a milestone to understand the mechanistic influence of CO₂ in the gasification. In order to avoid the complexities arising from the heterogeneous matrix of ligno-cellulosic biomass, this work also used pure cellulose and hemicellulose (*i.e.*, xylan), the main constituents of ligno-cellulosic biomass.

2. Material and methods

2.1. Preparation of sample and chemical reagents

Sub-bituminous coal was obtained from the U.S. and then pulverized using a Thomas Wiley Mill (USA) and the powder form of cellulose (Lot # 06526CJ) and xylan (Lot # 081M0025V) were purchased from Sigma Aldrich (St. Louis, USA). The coal is composed of 1.5% N₂, 89.3% C, 5.0% H, 0.8% S, and 3.4% O. The samples were stored in a sealed container at room temperature. High purity of N₂ and CO₂ was purchased from TechAir Korea (Seoul, Korea). Dichloromethane (Lot # MKBS5448V) for trapping condensable hydrocarbons was purchased from Sigma Aldrich (St. Louis, USA).

2.2. Thermo-Gravimetric Analysis (TGA)

TGA experiments were carried out in the N₂ and CO₂ environment using a Mettler Toledo TGA star system (Mettler, Switzerland). A series of TGA tests were carried out at a heating rate of 20 °C min⁻¹ over a temperature range of 20–900 °C. The flow rate of the purge (40 mL min⁻¹) and protective (20 mL min⁻¹) gas was a total of 60 mL min⁻¹, and 10 ± 0.02 mg of the sample was loaded into the TGA unit.

2.3. Tubular reactor setting

A tubular reactor (TR) was made of a quartz tube (Chemglass CGQ-0900T-13), and its outer diameter and length were 25.4 mm was 0.6 m, respectively. Stainless Ultra Torr Vacuum Fitting (Swagelok SS-4-UT-6-600, USA) was connected with the TR. A reactor scheme is shown in [Supplementary Information](#) (see Fig. SI-1). A sample of sub-bituminous coal was loaded into the center of the TR, and the sample loading mass was 3 ± 0.02 g of sub-bituminous

coal. In order to investigate the influence of CO₂ in the co-pyrolysis of sub-bituminous coal and ligno-cellulosic biomass, sub-bituminous coal was mixed with cellulose and xylan, separately. The experimental temperatures were provided from a split-hinged furnace. All gas flow rates were set using a Brooks mass flow controller (5850 series E). The pyrolytic oil was collected with a condenser equipped with a water circulation system at 4 °C.

2.4. Syngas and condensable hydrocarbon (tar) measurement

Effluents from the reactor were analyzed using a Micro GC (INFICON, Switzerland) for identification and quantification. The GC was equipped with a molecular sieve and Plot U columns. Calibration for the identification and quantification was conducted with standard gases purchased from the RiGas (Daejeon, Korea). Collected condensable hydrocarbon (*i.e.*, tar) was dissolved in dichloromethane (1:20 ratio dilution) and was measured with GC/MS-TOF (ALMSCO, UK) equipped with a capillary column (0.25 mm × 60 m, DB-WAX). The injection volume was 1 µL for each.

3. Result and discussions

3.1. Characteristics of the thermal degradation of coal in N₂ and CO₂

A series of TGA tests were conducted in N₂ and CO₂ at a heating rate of 20 °C min⁻¹ from 20 to 900 °C to characterize the thermal degradation of sub-bituminous coal, and the representative thermogram was illustrated in Fig. 1(a). In addition, a differential thermogram (DTG) in N₂ and CO₂ were incorporated with the representative thermogram in Fig. 1(a) to effectively differentiate the influence of CO₂ during the thermal degradation (*i.e.*, pyrolysis) of sub-bituminous coal.

The thermogram in Fig. 1(a) did not reflect the differences associated with the physical aspects in the thermal degradation of sub-bituminous coal in N₂ and CO₂; the onset and end temperature indicated that the thermal degradation in N₂ and CO₂ was nearly identical at the entirety of experimental temperatures (from 25 to 900 °C). This observation suggested that the direct reactions between sub-bituminous coal and CO₂ should be excluded: the direct influence of CO₂ on the sample surface of sub-bituminous is reflected by the different thermal decomposition rate shown as the slope in Fig. 1(a) since the direct reaction between sub-bituminous coal and CO₂ initiates the different thermal degradation rate. This could be also justified by the DTG curves from 25 °C to 600 °C in Fig. 1(a). However, the DTG curve in N₂ and CO₂ showed a very distinctive difference at temperatures higher than 800 °C. This observation is indicative of the Boudouard reaction (*i.e.*, C + O₂ → CO₂) [40]. One interesting observation was that the mass decay curves in N₂ and CO₂ (Fig. 1(a)) was not distinctive. This observation suggested that the reaction rate of the Boudouard reaction is very slow due to the heterogeneous reaction between the solid phase of carbon and the gas phase of CO₂. However, this mass decay could not be solely explained by the Boudouard reaction since the DTG curve at temperatures higher than 800 °C in N₂ also indeed showed a similar pattern in CO₂. Thus, this similar pattern at temperatures higher than 800 °C can be attributed to the simultaneous occurrence of the Boudouard reaction and dehydrogenation. However, a clear explanation of this was not possible at this stage.

For the further investigation into the influence of CO₂, the thermal degradation of biomass was characterized with cellulose and corn stover in CO₂ and the representative thermograms of cellulose and corn stover were illustrated in Fig. 1(b). In order to avoid complexities, the thermograms of cellulose and corn stover in N₂ were

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