



Enhanced accessibility of carbon in pyrolysis of brown coal using carbon dioxide



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ABSTRACT

This work investigates the effect of CO₂ in pyrolysis of brown coal (also referred to as lignite). CO₂ changes the distribution of pyrolytic products of brown coal. More CO is generated for the pyrolysis of brown coal in CO₂ than that in N₂. Differential scanning calorimeter (DSC) experiments show that the pyrolysis of brown coal in CO₂ is more exothermic than that in N₂. This may indicate that the enhanced generation of CO is attributed to an enhanced thermal cracking induced by CO₂. The more generation of CO for the reaction in CO₂ (4.2 mol.% at 700 °C) than in N₂ (0.5 mol.% at 700 °C) is a result of shifting carbon distribution from condensable hydrocarbons (e.g., tar) to CO. In addition, more CO is generated from the pyrolysis of brown coal in CO₂ than pyrolysis of sub-bituminous coal. This study signifies that low-rank coal can be effectively used as an energy source when CO₂ is employed during pyrolysis process.

1. Introduction

Fossil fuels have played a dominant role in the global energy system and global energy production and/or consumption have continuously increased [1,2]. The total energy consumption and/or production reached up to 520 EJ in 2017 [3]. Despite the fact that fossil fuel energy has positively contributed to the human development, it has led to adverse environmental impacts as the major source of local and regional air pollution and global warming [4,5]. In particular, the anthropogenic carbon emissions from fossil fuels combustion (oxidation) has already exceeded the full capability to assimilate carbon *via* the natural carbon cycle, which is pointed out as one of key factors triggering climate change [6]. Therefore, low-/non-carbon energies (e.g., waste-to-energy, photovoltaic energy, solar energy, wind energy, tidal energy, geothermal energy, etc.) and carbon neutral energies (e.g., biodiesel, bioethanol, biogas, biohydrogen, etc.) have been developed extensively over the last two decades [7,8].

Even with the potential of low-/non-carbon energies in relation to reduction of our heavy reliance on fossil fuels, fossil fuels (coal, oil, and gas) still serve a primary/dominant source for carbon in the chemical

industry [9,10]. A common misconception about the energy and chemical industry – regarding the energy and chemical industry as a separated sector – prevails among many people [11]. Indeed, the energy industry is the subordinate concept of the chemical industry, accounting for at the most 30% of the chemical industry [11]. Considering the fact that social metabolisms for carbon are proportional to life quality, carbon demand that sustains the chemical industry is expected to increase [12,13]. Thus, the term of “sustainability” is profoundly contingent on how and/or where we procure carbon sources without environmental burdens [14,15]. In this respect, carbonaceous materials, such as biomass and coal, can be a promising carbon source due to their intrinsic carbon neutrality and abundance, respectively [16,17]. However, to employ carbonaceous materials for the current chemical industry, carbonaceous materials must be transformed into gaseous/liquid carbons because the current platform of the chemical industry is equipped to change gaseous/liquid carbons into desired chemicals with/without using catalysts [18,19]. For example, on the contrary to the case of using petroleum and natural gas as the carbon source for the chemical industry, the additional unit processes for transforming carbonaceous materials into gaseous/liquid carbon are

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required, which implies that more CO₂ is generated due to the thermodynamic inefficiency of each unit operation process [20,21]. Thus, developing energy and cost-efficient technologies to transform carbonaceous materials into the gaseous/liquid form of carbons are of importance. More preferably, developing a new platform using CO₂ as an initial feedstock to convert carbonaceous materials into gaseous/liquid carbon is highly desirable [22,23]. It can be a solution for the ultimate carbon management, neither deteriorating life quality based on carbons nor exacerbating environmental problems through using CO₂ [24,25].

Thermo-chemical processing of coal will have continued to play a crucial role in the future. Nevertheless, the processes can emit toxic air pollutants [26,27]. Thus, efforts must continue to be intensified to develop advanced thermo-chemical technologies for clean utilization of coal with near-zero emissions of toxic byproducts and a high efficiency of recovering energy. Although thermo-chemical processes of coal have been widely studied, the effect of CO₂ on pyrolysis of low-rank coal has rarely explored. Within this context, we laid great emphasis on pyrolysis of brown coal (lignite) since lignite accounts for 45 wt.% of the world total reserve [28]. To enhance the carbon accessibility to gaseous carbon sources such as CO, the role of CO₂ in pyrolysis of brown coal was principally investigated in this study. For an in-depth investigation, pyrolysis of brown coal in N₂ and CO₂ was characterized thermogravimetrically. To assess the more realistic data, a laboratory-scale pyrolysis of lignite was conducted. All products (char, pyrolytic gases, and oils) from the pyrolysis of lignite in N₂ and CO₂ were compared to figure out the mechanistic roles of CO₂. To do so, this study justified that low-rank coal such as lignite (brown coal) can be a promising carbon source rather than high-rank coal such as anthracite and sub-bituminous coal. This study experimentally proved that the usefulness of lignite could be synergistically enhanced by using CO₂ as reaction medium and feedstock since the accessibility of solid-state carbon to carbon monoxide (CO) was enhanced, which maneuvered the carbon distribution from pyrolytic oil to syngas. Therefore, the scope of this study was limited to pyrolysis of lignite because pyrolysis (pyrolysis) is an intermediate step for the gasification process. Lastly, the reaction kinetics for CO₂ in pyrolysis of brown coal (lignite) was figured out by the amount of CO₂ varying.

2. Materials and methods

2.1. Chemical reagents and sample preparation

Sub-bituminous coal and lignite (brown coal) were obtained from Korea Institute of Geoscience and Mineral Resources (KIGAM). The sub-bituminous coal is composed of 1.5 wt.% N, 89.3 wt.% C, 5.5 wt.% H, 0.8 wt.% S, and 3.4 wt.% O. The particle size of two coal samples was controlled using a ball mill, and the average sample size was adjusted to 0.1 mm. The proximate analysis of brown coal was conducted using a muffle furnace (FX-14, DAIHAN Scientific) in accordance with the literature [29]. The ultimate analysis was also conducted with an elemental analyzer (Flash 1112, Thermo Scientific). All measurements from the proximate and ultimate analysis of brown coal are summarized in Table 1. Prior to an experiment, each coal sample was dried at 70 °C for 4 h to remove any moisture. High purity N₂ and CO₂ gases were purchased from TechAir. Dichloromethane was purchased from Sigma Aldrich.

Table 1
Proximate and ultimate analysis of brown coal.

	Proximate Analysis (wt.%)				Ultimate Analysis (wt.%)					
	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	O	N	S	Ash
Brown Coal	14.81	40.36	37.96	6.87	68.31	4.77	16.36	1.37	1.12	8.06

2.2. Thermo-gravimetric analysis (TGA)

A series of TGA experiments was conducted in the N₂, CO₂, and air circumstances. All TGA experimental works were carried out using a TGA unit (STA 449 F5 Jupiter, Netzsch) to figure out the effect of CO₂ on the thermal decomposition of coal. The TGA test was conducted (heating rate of 10 °C min⁻¹ from 30 to 900 °C.) The flow rate was controlled by the three mass flow controllers that was equipped in the TGA unit. The total flow rate was 80 mL min⁻¹ (protective gas (N₂): 20 mL min⁻¹ and purge gas (N₂, CO₂, or air): 60 mL min⁻¹). The sample loading of the coal sample was 10 ± 0.01 mg. The TGA tests were carried out in triplicates. In addition, prior to the TGA test, the reference test (i.e., running TGA with no sample) was done to subtract the buoyancy effects.

2.3. Laboratory-scale pyrolysis experiment of brown coal

For a laboratory-scale pyrolysis experimental work, a batch-type tubular reactor (TR) was constructed, as shown in supporting information (Fig. S1). A quartz tubing (CGQ-0900T-13, Chemglass) was employed as a main body of the TR, and its dimension was 25.4 mm of the outer diameter as well as 0.6 m of length. Ultra Torr Vacuum Fitting (SS-4-UT-6-600, Swagelok) was used to connect the gas flow system. A reducing union fitting was used to connect the gas flow system. A programmable tubular furnace was used to control pyrolysis temperature. The TR was secured in the tubular furnace, and the sample loading for each run of the pyrolysis of coal was 3 ± 0.05 g. K-type thermocouples (Omega) were placed at above of the coal sample, and the temperature deviation for each pyrolytic run was adjusted less than ± 3 °C. The flow rate of N₂ and CO₂ was varied from 100 to 500 mL min⁻¹, and all experiments were done at an ambient pressure. The flow rate was controlled by a mass flow controller (5850 series, Brooks Instrument). The effluents from the TR was directly hooked up to a micro-GC (INFICON 3000A). Prior to gas analysis, the condensable hydrocarbons were trapped at -20 °C using a chiller.

2.4. Analysis of syngas and condensable hydrocarbons (tar)

The gaseous effluent from the TR unit was analyzed with the micro-GC. A molecular sieve column and plot U column was equipped in the micro-GC. The GC was calibrated using a standard gas mixture (RIGAS). Collected condensable hydrocarbons (pyrolytic oil and/or tar) were diluted with dichloromethane (1:20 dilution ratio), and condensable hydrocarbons were qualified using CG/MS-TOF (ALMSO, UK) equipped with a capillary column (0.25 mm × 30 m, HPMS-5). The injection volume was 1 μL.

3. Results and discussion

3.1. Pyrolysis of brown coal in N₂ and CO₂

To characterize thermal degradation of brown coal in the N₂, CO₂, and air circumstances, a series of the TGA tests was conducted at a heating rate of 10 °C min⁻¹ from 30 to 900 °C. Mass decay of brown coal in N₂, CO₂, and air conditions is presented in Fig. 1. Their corresponding thermal degradation rates in N₂, CO₂, and air are also

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