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Effect of CO_2 on the characteristics of soot derived from coal rapid pyrolysis

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ABSTRACT

The present work aims to investigate the effects of a CO_2-rich atmosphere on the characteristics of coal-derived soot. The rapid pyrolysis of Shenfu bituminous coal was conducted in a Drop tube furnace (DTF) in N_2 and CO_2 atmospheres with a wall temperature of 1073–1473 K and residence time below 700 ms. The yields and microstructure characteristics of N_2-soot and CO_2-soot were analysed by using a series of techniques (elemental analysis, HRTEM, Raman, XRD, FT-IR and thermogravimetry techniques). CO_2 enhanced the soot formation and proceeded the dehydrogenation. CO_2 improved the order of internal carbon lattices, enhanced the lateral extension of carbon nanostructures, decreased the interplanar spacing of the graphene layers and also promoted the stack of polyaromatic layers. The variations of the SOLO, DUO, TRIO and QUARTO structures were also analysed, and the contribution of CO_2 was found to reduce the defects of the basic structure units (BSU). The defects of soot were an important indication of the initial gasification reactivity. Overall, CO_2-soot was more mature and low active than N_2-soot.

1. Introduction

Coal is widely used for combustion and is expected to be a crucial source for power generation in the next several decades [1]. The submicroscopic soot particles produced during combustion promote heat transfer because of their radiative heat-transfer effect [2]. In combustion, the burnout time and burnout rate are more or less determined by the soot reactivity because coal-derived soot reacts much more slowly than the corresponding char in an oxidizing atmosphere [3–5]. The elimination of soot is important to the particulate matter (PM) control because soot usually contains large amounts of adsorbed polyaromatic hydrocarbons (PAHs) [6,7]. To increase the carbon conversion and optimize the combustion process, the characteristics of soot should be investigated in detail [4,8].

Many previous works have revealed information about the formation of coal-derived soot. Soot formation consists of 5 main stages: nucleation, surface growth, coagulation, agglomeration and aggregation [9]. It is widely acknowledged that tar and volatiles partly evolve into soot in the initial combustion stage (pyrolysis stage) via secondary reactions at high temperature (>1200 K) [5,10–12]. As expected, coal with a high tar yield usually has a high soot yield. Polymerization and thermal cracking are two main competitive pathways for primary tar during the rapid pyrolysis of coal [13]. The temperature dependency of the soot yield is described as a bell-shaped curve, and the soot yield maximizes at approximately 1600 K [14]. Traditionally, molecular-PAH chemical condensation was considered as the main pathway of soot formation, but Russo and Ciajolo [15] recently proposed a new soot formation theory: the physical coagulation of small PAHs with odd-numbered rings and/or sp^3 bonds.

Soot microstructures have also drawn much attention in early studies. Galvez et al. [16] found that soot nanoparticles consist of non-stacked (single layers) or partially stacked layers. Many dislocations and lattice defects are presented in soot particles [17]. The SOLO, DUO, TRIO and QUATRO structures were qualitatively analysed by Centrone et al. [18]. Several factors that affect soot reactivity have been identified: particle size, graphitization degree of microstructures, mineral content, etc. [4,19,20].

It should be emphasized that in most of the aforementioned literatures, soot was prepared in an N_2 atmosphere. Because coal particles experience rapid pyrolysis in CO_2-rich atmospheres during oxy-fuel combustion, knowledge about soot formation in the CO_2-rich atmosphere is required to identify the possible chemical effect of high CO_2 levels on the soot characteristics. Although many previous studies [21–26] have revealed that the pyrolysis products (both gas and char) obtained in CO_2 atmospheres significantly change compared to those obtained in N_2 atmospheres, few works

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Nomenclature

d_{002}	interplanar spacing of graphene layers (nm)
L_a	Graphene layer size (nm)
n	number of Graphene layers
Pos(G)(and Pos(D))	G peak position (and D peak position)

Abbreviation

DTF	Drop tube furnace
PM	Particulate matter
PSDs	Particle size distributions
BSU	Basic structure units
PAHs	Polyaromatic hydrocarbons
HRTEM	High-resolution transmission electron microscopy
SEM	Scanning electron microscope
FT-IR	Fourier transform infrared spectroscopy
TGA	Thermogravimetric analyser
OPLA	Aromatic out-of-plane C–H bending
XRD	X-ray diffractogram

focused on the soot obtained in a CO_2-rich atmosphere. The effects of CO_2 on soot formation have been addressed with controversial results in the few available studies. Morris et al. [27,28] measured lower soot emissions under oxy-fired conditions than under conventional air conditions. Ma [17] believed that oxygen-containing species would attack the PAHs of the soot precursor and rupture the aromatic ring structures. Guo and Smallwood. [29]. believed that the CO_2 addition would suppress the soot formation by reducing the H radical concentration. However, Apicella et al. [30] found that soot was significantly more abundantly formed in CO_2 than in an N_2 flow. Further detailed information about the effects of CO_2 on soot microstructures is necessary.

The effect of the pyrolysis atmosphere (N_2/CO_2) on the soot characteristics was mainly studied here using soot from the DTF. In particular, information about the soot microstructures as a function of residence time was first acquired in this work using the newly developed DTF. The gasification reactivity of soot was assessed, and its relationships among the microstructure defects were also investigated.

2. Experimental

2.1. Coal samples

Soot samples were obtained from the rapid pyrolysis of Shenfu bituminous coal (SF-coal) in N_2-rich and CO_2-rich atmospheres. The coal samples were ground to 90–150 µm and dried at 378 K for 12 h before the pyrolysis experiment. The properties of SF-coal are listed in Table 1.

2.2. Pyrolysis apparatus

Coal pyrolysis experiments were conducted in a newly developed experimental-scale laminar drop tube furnace (DTF) in both N_2 and CO_2 atmospheres. The experimental apparatus of DTF is shown in Fig. 1. The boron nitride conductive ceramic crucible, which was installed in the quartz tube, was heated by a 35-kHz high-frequency current and maintained at a uniform temperature. The crucible temperature was controlled at 1073–1473 K by adjusting the electric current. The temperature distribution of coal particle is shown in Supplementary data. The residence time of coal particles that passed through the isothermal zone could be changed by adjusting the boron nitride conductive ceramics (30, 60, 90, 120 and 150 mm). The residence times at varied temperatures were calculated by Navier–Stokes equations (see Supplementary data). Pyrolysis gas (N_2 and CO_2) flowed into the DTF from the top of the quartz tube.

There were mainly four sampling positions for the DTF apparatus. Position A denoted the inner wall of top and middle quartz tube. Position B denoted the inner wall of bottom quartz tube. Position C denoted the sampling bottle, and Position D denoted the sampling bottle connected to the infundibular bottom quartz tube. The distinction of products sampled from different positions is shown in Supplementary data.

The soot from Position A are formed under the same conditions with soot from Position B and Position C. thus, the pure soot samples collected from Position A were regarded as representative fractions in characterization. The fluffy soot samples were scraped from position A and labelled the denominations: (L)-(T)-(N_2 or CO_2), where L and T denote the length of the isothermal zone and the pyrolysis temperature, respectively. For example, 150-1473-CO_2 denotes the soot samples derived from the coal pyrolysis in the CO_2 atmosphere with an isothermal zone of 150 mm and a wall temperature of 1473 K.

A yellowish deposit (tar) was found on the wall of the bottom quartz tube (Position B) after the rapid pyrolysis of SF-coal. The tar yield was acquired by mass difference method. The yield of fine solid products (small char fragments and soot) carried by gas flow to Position C was obtained by mass difference method and those fine particles were poured out for further analysis. The coarse solid products, which comprised of abundant char and slight soot, were sampled from the sampling bottle (Position D). The yields and characteristics of products sampled from Position C and Position D are shown in Supplementary data.

Yield of soot consisted of three parts: soot scraped from Position A, soot from Position C and soot from Position D. The soot mass ratios from Position C and Position D were determined from volume basis fractions derived from particle size distributions (PSDs). The density separation method was proved to be reliable in previous literatures [5,19]. More detailed information about the calculation of total soot yield is shown in Supplementary data. The yields of soot and tar were calculated based on the coal dry ash free basis.

2.3. Characterization of soot samples

The soot samples were analysed using an element analyser (Vario MACRO CHN/CHNS) and the ASTM-D5373 method [31]. The morphology of soot aggregates was observed using a field emission scanning electron microscope (FESEM, Hitachi S4800). The PSDs of products sampled from different positions were measured by laser particle analyser (Mastersizer 2000).

Table 1
Properties of Shenfu bituminous coal.

Proximate analysis. w_d %			Ultimate analysis. w_d %					Average diameter. d_s / µm	Density. ρ_s / $m^3\ kg^{-1}$
V	Fc	A	C	H	N	S	O*		
35.48	59.06	5.46	76.85	4.63	1.23	1.34	10.49	117.3	1500

*: Calculated by difference.