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Experimental analysis of the evolution of soot structure during CO_2 gasification

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ABSTRACT

The morphology and nanostructure evolution during gasification was examined for a coal-derived soot and, to permit comparisons to other research, two carbon black samples. The investigation examined four different conversion extents at 1273 and 1473 K. The primary particle diameter decreased significantly during the initial stage and then changed slowly. The gasification behavior varied with the initial nanostructure and treatment temperature. At 1273 K the consumption behavior followed a hybrid mode comprised of shrinking core and homogeneous reaction models. However, at 1473 K, a previously unobserved gasification behavior occurred with the soot forming concentric spheres. Here the gasification progressed by initially forming micropores, followed by insufficient permeation of oxidant with the subsequent consumption of the core, ultimately forming hollow particles. Raman spectra and X-ray diffraction patterns indicated there was a transformation from initially ordered to less well-ordered structure. Partial gasification induced disordering to different extents, accompanied by a slight maturing associated with thermal annealing. The crystallites were preferentially consumed along the graphitic edges for coal-derived soot. At the start of gasification, the density of the soot increased but subsequently declined. Abundant micropores with multimodal distributions were newly generated and continually developed during gasification.

1. Introduction

Gasification has been widely applied for the production of fuels and chemicals [1]. Abundant soot is formed as an undesirable byproduct during coal gasification [2–4]. The soot structure is generated with a less ordered core and a large number of polyaromatic hydrocarbons (PAHs) surrounding nucleation points. Soot particles are a significant health hazard due their fine size [5–8] and carcinogenic PAH surface components. Soot is also a climate change forcing agent. Therefore the subsequent gasification of soot is of great significance for utilization efficiency and pollution control [9,10]. Significant chemical and physical transitions can occur during oxidation/gasification [11,12]. Improving soot evolution knowledge will aid in strategies to minimize soot emissions within gasifiers. In addition, it will also aid in getting better conditions of soot-catalyst contact that are crucial to the performance of catalytic filters for diesel particulate abatement [13,14].

Varied measurements for gasifier soot can help analysis the exact gasification model. Numerous analytical approaches have been used to evaluate soot structure. High-resolution transmission electron microscopy (HRTEM) is widely used to investigate parameters such as diameter [15], lattice fringe tortuosity [7,16] and length distributions [17]. Raman spectroscopy and X-ray diffractograms provide a convenient way to quantify the structural ordering [18,19].

Soot morphology and structural transformation during oxidation have been examined previously. Vander Wal et al. [20] investigated diesel soot via HRTEM and observed some hollow particles with graphitized outer shells. The authors found that partial oxidation induced soot graphitization but with different propensities depending on soot precursor. Jaramillo et al. [6] quantified soot oxidation kinetics under different pressures. They hypothesized that the oxidant permeated the outer portions of the soot particles and subsequently caused the breakup of the initial graphene segments. Ghiassi et al. [21] found internal consumption in an O_2 atmosphere was higher for particles $<$ 10 nm compared to larger particles. Ivleva et al. [18] reported that a steep initial decrease in the relative intensity in the D3 band was explained by the rapid preferential oxidation of a reactive amorphous carbon fraction. Recently, soot generated during gasification has been examined. Using an industrial gasifier, Wiinikka et al. [11] observed

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Nomenclature

SF-soot	soot derived from rapid pyrolysis of ShenFu bituminous coal
HRTEM	High-resolution transmission electron microscopy
XRD	X-ray diffraction
PAHs	Polyaromatic hydrocarbons
DTF	Drop-tube furnace
SOF	Soluble organic fraction
SCM	Shrinking core model
HRM	Homogeneous reaction model
BET	Brunauer-Emmett-Teller model
BJH	Barrett-Joyner-Halenda model
DFT	density functional theory model
x	Conversion of soot during gasification
d_{002}	Interlayer spacing of crystallites/nm
L_c	Crystallites thickness/nm
L_a	Crystallites basal plane diameter/nm
n	Average number of layers
I_D/I_G	Ratio of the integrated intensities of the D and G bands

less-ordered soot particles were present at higher temperatures. Qin et al. [22] found a lower soot yield in a gasification environment than under pyrolysis conditions. In later work [23], they also found that the shape of the particles changed from spherical to irregular crystals with an increasing steam/carbon molar ratio.

The differences in behaviors will impact the particle density. However, only limited experimental data is available for density transitions during oxidation. Thus density is usually assumed to be constant during consumption [24–26]. However, Yamaguchi et al. [27] showed that the soot density increased during soot formation but decreased during oxidation. Coupled to the density is the evolution of porosity and transitions in the pore size distribution accompanying oxidation [20,28–30]. Smith et al. [31] attributed a 6-fold increase in the surface area during carbon black gasification to porosity development, while Du [32] speculated that the rapid increases in the CO_2 surface area were due to consumption opening previously closed pores.

Unfortunately, the transformations in structural evolution are seldom examined (previous work primarily examined single conversion extents). How the structure evolves during gasification remains unclear. In addition, the gasification of coal-derived soot, which is known to differ structurally from diesel soot, has been mostly overlooked. In this work, the gasification of SF-soot (soot derived from the rapid pyrolysis of ShenFu bituminous coal) with various conversions was examined. The evolution of the structural characteristics (morphology, nanostructure, helium density, and pore structure) during gasification was quantified with different behaviors being observed at a low and high temperature for this coal-derived soot. This included the formation of a novel concentric spherical structure that was previously unknown. To better relate the observations here to the literature, two carbon blacks were similarly evaluated.

2. Materials and methods

2.1. Soot samples

SF-soot was derived from the rapid pyrolysis of ShenFu bituminous coal in a drop-tube furnace (DTF) with a wall temperature of 1573 K and a residence time of 744 ms [33]. This coal is used for gasification commercially in China. The carbon black samples were commercially obtained. The N330 is derived from coal tar and N990 has a particle diameter similar to that of SF-soot (~200 nm). These were selected to provide a comparison with literature observations. The properties of SF-coal and the soot samples are provided in the Supplementary data. The soot samples were essentially ash-free.

2.2. Gasification apparatus

The partially gasified soot was acquired from isothermal gasification experiments conducted in an experimental-scale fixed-bed reactor. Oxygen was removed with a N_2 purge for 10 mins. The samples were heated to either 1273 or 1473 K using a 35-kHz high-frequency current for < 2 min. under an N_2 atmosphere. The gas flow was switched to CO_2 when the desired temperature was achieved. These temperatures were selected to provide a range of behaviors within the reactor system limitations. Partially gasified soot with conversions of ~0.2, 0.4, 0.6, and 0.8 were prepared in the fixed-bed reactor at 1273 and 1473 K. The details (gasification temperature, duration, and conversion extent) of the 24 gasification tests are shown in Table 1. The gasification duration for each desired conversion was estimated initially from thermogravimetric analysis data. The conversion, x, in the fixed-bed reactor was calculated from Eq. (1):

$$x = \frac{m_0 - m}{m_0} \tag{1}$$

where m_0 and m are, respectively, the initial and instantaneous masses of the soot during gasification.

The partially gasified soot samples were named with the convention N-T-C, where N denotes the soot, T the fixed bed reactor temperature, and C the fractional conversion. For example, SF-soot-1273-0.18 denotes partially gasified soot derived from SF-soot at 1273 K, to a conversion of 0.18 Fig. 1.

2.3. Characterization of the soot samples

Raman spectroscopy and X-ray diffraction (XRD) were used to investigate a carbon's structural evolution during gasification. The equations for calculating the crystallite parameters are shown in the Supplementary data. The Raman spectrum was recorded using a Thermo Fisher DXR microscope with a 455 nm He-Ne laser (3 mW) and a 100× bjective optical microscope. High-quality Raman spectra were obtained by 50 scans coadded at a resolution of 0.5 cm^{-1} in the range of 100–3500 cm^{-1} for three regions. The crystallites of the soot were also characterized by using an X-ray diffractometer (D/max-2550 VB/PC, RIGAKU) with Cu radiation (ASTM-D5187 [34]). The diffraction patterns were recorded in the 2θ range of 10-80° (resolution 0.02°) for three regions.

The HRTEM micrographs were obtained using a JEOL JEM-2010. This approach provided information regarding the morphology and

Table 1
Details of gasification test.

	1273 K		1473 K	
Soot precursor	Duration/min	Conversion	Duration/min	Conversion
SF-soot	15.0	0.18	1.9	0.21
	35.5	0.43	4.2	0.43
	55.0	0.61	6.4	0.62
	80.0	0.78	8.5	0.83
N330	25.0	0.19	2.5	0.21
	55.0	0.37	4.5	0.42
	90.0	0.62	7.0	0.63
	125.0	0.83	9.0	0.82
N990	6.5	0.19	0.9	0.19
	12.0	0.37	1.5	0.43
	20.0	0.59	2.4	0.58
	28.5	0.79	3.6	0.82