Variation of the coal chemical structure and determination of the char molecular size at the early stage of rapid pyrolysis

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Tongmin Cui, Wenke Fan, Zhenghua Dai, Qinghua Guo, Guangsuo Yu, Fuchen Wang *

Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, Shanghai Engineering Research Center of Coal Gasification, East China University of Science and Technology, Shanghai 200237, PR China

HIGHLIGHTS

- Rapid pyrolysis experiments were carried out for a short duration.
- Char chemical structure was characterized by five parameters based on IR spectrum.
- Equivalent diameter of monomer D_C was proposed to study the char molecular size.

GRAPHICAL ABSTRACT
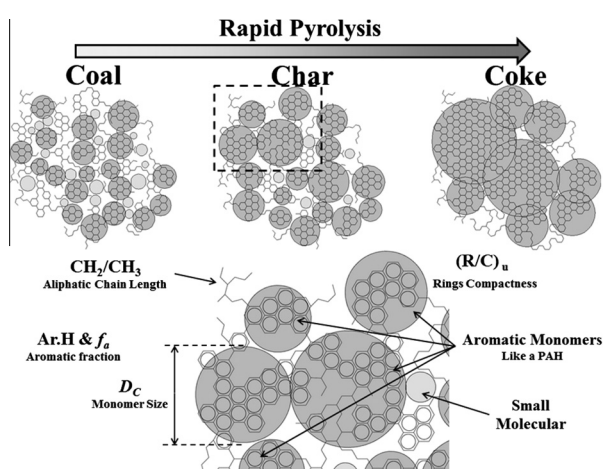
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ABSTRACT

Rapid pyrolysis ($\sim10^4$ K/s) experiments investigating lignite, bituminous coal and anthracite were conducted to study the effect of the thermal process on the coal structure. The interest was focused on the chemical structure variation occurring at the early stage of pyrolysis (0–500 ms) and high temperature (1173–1773 K), which includes the mass loss ratio, volatile content, element content and organic groups. A series of parameters was used to characterize the chemical structure, CH_2/CH_3 ratio, fraction of aromatic hydrogen and aromaticity (f_a). The char's molecular size was determined based on both ring condensation degree $(R/C)_u$ and equivalent diameter of the aromatic monomer (D_C). This result demonstrated that these five chemical structural parameters (CSPs) increase with the pyrolysis time and temperature. The comparison of three types of coals reveals that the CSPs of lignite are lower and increase faster than those of bituminous coal and anthracite.

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1. Introduction

An increased interest in clean coal technology (CCT) has impelled recent studies toward coal gasification technology [1–6]. Rapid pyrolysis, which is a complex physical and chemical process that occurs as the initial stage in coal combustion and gasification [7–9], plays a major role in most coal conversion processes [10]. Coal is known as a heterogeneous mixture consisting primarily of a complex polymer network of organic components [11], and its chemical structure rapidly change during the thermal process [12–16]. These variations in a molecular or lattice scale

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Nomenclature

L_a	ash-tracing mass loss ratio per gram of dry coal, (g/g)
CH_2/CH_3	Absorbance area ratio of CH2 and CH3 in the FT-IR spectrum
$C(i)$	concentration of absorbing species i, (mg/cm^2)
$a(i)$	integral absorptivity of absorbing species i, (cm^2/mg)
$A(i)$	normalized integral area of absorbing species i
$f(i)$	mass fraction of species i
f_a	aromaticity
H/C	molar ratio of hydrogen and carbon, (mol/mol)
O/C	molar ratio of oxygen and carbon, (mol/mol)
$(R/C)_u$	ring condensation degree
D_C	equivalent molecular diameter, (nm)
A	area of projection of a molecule, (nm^2)

P	perimeter of the projection of a molecule, (nm)
L_C	bond length of C–C in an aromatic ring, 0.139 nm, (nm)
L_H	average distance between adjacent hydrogen atoms, (nm)
L_{C-H}	bond length of C–H in an aromatic groups, 0.108 nm, (nm)

Abbreviation

PAH	polycyclic aromatic hydrocarbon
CSP	chemical structural parameter
H_{ar}, H_{al}	hydrogen in aromatic (or aliphatic) groups
H-H$_{OH}$	hydrogen not including H in OH groups
C_{ar}, C_{al}	carbon in aromatic (or aliphatic) groups

(0.1–10 nm) significantly affect the conversion efficiency of the combustion and gasification. A series of parameters have been proposed to characterize the coal chemical structure. CH_2/CH_3, which represents the ratio of C—H bond in methylene to methyl, is related to the length of aliphatic chains [11,17,18]. Both fraction of hydrogen present as aromatic (H_{ar}) and aromaticity (f_a) are parameters to describe the coal structure transformation [19], which is closely connected to the ratio of aromatic and aliphatic contents in coal. The ring condensation degree $(R/C)_u$, which represents the condensation extent of carbon rings in the coal molecular structure, is defined as the number of rings of atomic carbon in a monomer [17]. All of these parameters represent the organic chemical structure and they have been used to analyse coal pyrolysis, extraction and coalification [16,20–26].

Several analytical methods have been applied to determine these parameters and measure the coal chemical structure [27]. Raman spectroscopy [28–30] and X-ray diffraction (XRD) [26,29,31,32] have been applied to analyse the crystalline structure of carbon in the high-rank coals. Nuclear magnetic resonance (NMR) [18,33–35] and Fourier transform infrared spectroscopy (FT-IR) [11,16,18,22–24,26,36,37] have been used in low-rank coal analysis because of their excellent identification of different organic groups. In addition, infrared spectroscopy appears to be the common method to obtain the structural parameters because of its easy operation and low cost [11,16,24]. The KBr pellet methodology is frequently used in quantitative infrared studies of coal based on Solomon's measurement of aromatic and aliphatic groups [38].

The investigation of the chemical structure of coal can help to predict the thermal behavior, such as the gasification/combustion reactivity [39]. The reactivity of char with CO_2/O_2 is closely related to the monomer carbon crystalline size of coal/char [40,41]. Although many studies have focused on the variations of the coal chemical structure, no suitable parameter appeared to directly characterize the molecular size of char [42]. Herein, D_C was defined and calculated as the equivalent molecular diameter of a char monomer. In addition, the rapid pyrolysis at high temperature has been observed to be a chemical process with the temporal scale of milliseconds to seconds [12,43–45]. However, the literature has seldom paid attention to the variation of the coal chemical structure at the millisecond time scale.

The main purpose of this work was to investigate D_C and other CSP variations at the early stage of rapid pyrolysis. The effects of the pyrolysis temperature, time and coal property were studied, and the KBr pellet IR spectroscopy method was used. In addition, some works considered that the catalytic effect of ash would dominate the low-temperature thermal process (usually below 1173 K) [46]. The pyrolysis was varied from 1173 to 1773 K to investigate the effect of the coal rank and the active components in ash (such as alkaline and alkaline earth metal) that lost their catalytic effect because of volatilization and inactivation.

2. Experimental

2.1. Coal sample

Three types of coals of different ranks were used in this study. Lignite originated from Erdos, Inner-Mongolia, China, bituminous coal originated from Yulin, Shaanxi, China, and anthracite originated from Jincheng, Shanxi, China. The coal was ground to powder and dried at 378 K for 2 h. The ASTM-D5142 (proximate analysis), ASTM-D5373 (C, H & N analysis) and ASTM-D4239 (S analysis) methods [47–49] were used in the proximate analysis and ultimate analysis of coals (Table 1) and their semi-chars. Other physical characteristics and ash composition are also shown in Table 1 (the alkaline content was calculated in reported method [46]).

The infrared spectroscopy (IR) analysis was used to determine the organic groups in coal and char [50]. The differences in IR spectra of raw coal (Fig. 1) indicate that the contents of the functional groups vary with the coal properties.

2.2. Pyrolysis apparatus and procedure

Coal pyrolysis was performed in a quartz tube reactor, inside which a molybdenum cylinder was sealed as the crucible. The high-frequency current of 35 kHz was generated and formed a quickly mutative magnetic field in the axial direction of the molybdenum. The temperature of the molybdenum remained at 1173–1773 K because of eddy current heating. The residence time of pyrolysis was varied by changing the cylinder height to 30, 40, 60, 80, 100, 125, and 150 mm. A thermocouple bead was pointed to 20 mm above the bottom edge of the crucible to measure the gas temperature in the crucible, which was characterized as the pyrolysis temperature.

A dust generator was used to feed the particles into the reactor (Fig. 2b). The feeding rate (0.5 g/min) was controlled by the lifting rate of piston, which was driven by a step motor. The inert gas flowed into the reactor from the top of the quartz tube at 300 mL (STP)/min. The coal particles dropped through a thin tube (400 mm length; 8 mm i.d.) into the reaction zone. The solid products were collected at the bottom of the tube. The pyrolysis temperature was controlled in the range of 1173–1773 K. The residence time of particles was calculated using Navier-Stokes