Fuel Processing Technology 178 (2018) 139–147

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Structure, electrical conductivity, and dielectric properties of semi-coke derived from microwave-pyrolyzed low-rank coal

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ARTICLE INFO

Keywords:
Low-rank coal
Microwave
Structure
Resistivity
Dielectric property

ABSTRACT

A study was undertaken to investigate the structure, electrical conductivity and dielectric properties of low-rank coals during microwave pyrolysis. The mechanism of dielectric response during microwave pyrolysis was also discussed. The pyrolysis conditions were a microwave power of 800 W and different radiation times; dielectric properties were measured using a vector network analyzer at a frequency of 2450 MHz, and the electrical conductivity was measured using a four-probe resistivity tester. Results show that with increasing microwave radiation time, the functional groups gradually cracked and fell off, and the structural order was gradually enhanced. In addition, the order of the structure increased the number of sp^2-hybridized carbon atoms on a single plane and increased the delocalized electrons between the graphite crystal planes. The complex relative permittivity and resistivity of the semi-cokes exhibited a significant dependence on microwave radiation time and pyrolysis temperature, especially after 15 min of microwave radiation. By comparing the calculated and measured values of imaginary parts, it could be deduced that the electric conductive loss is also an important part of the microwave attenuation mechanism in the process of microwave pyrolysis, as important as the relaxation loss and the interface polarization loss.

1. Introduction

The utilization of low-rank coal is limited due to the higher level of moisture content and low heat value [1]. The coal-staged conversion technology (coal conversion by grade and quality) is one of the promising way for low-rank coal utilization, since it can make the best use of the coal components. Under the mild conditions, the gas, tar and semi-coke (char) are obtained at medium-to-low-temperatures and low pressures [2,3]. The gas could be used for power generation, while the tar produces fine chemicals after deep processing. The large amount of semi-coke, the clean solid fuel, is expected to be used for gasification and civil burning. [4,5]

Pyrolysis is the core technology of coal-staged conversion. Up to now, different technologies and facilities for coal pyrolysis have been developed. However, the traditional heating methods has the disadvantages of slow heating velocity, uneven heating, and low efficiency. Therefore, it is necessary to develop new heating technology to support coal-staged conversion.

Microwave (MW) heating technology has the advantages of selective heating, uniform heating, and high efficiency. Recently, it has attracted widespread attention in many industry fields, and is expected to be more convenient to realize staged conversion of low-rank coal. [6–9]

MW belongs to high-frequency electromagnetic waves, and the frequencies of 915 and 2450 MHz are commonly used in industry [7]. In the MW field, the dielectric material consumes the MW energy in the form of dielectric loss and then produces heat. It is generally believed that dielectric loss is mainly caused by typical relaxation and interfacial polarization for low-rank coal. The dielectric properties [10] determined by the polarization characteristics of the dielectric material, can be represented by the complex relative permittivity composed of real and imaginary parts, which are given by [7,11,12]

$$\varepsilon_r = \varepsilon_r' - i\varepsilon_r', \quad (1)$$

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'}. \quad (2)$$

As indicated by Eq. (1), the complex relative permittivity is comprised of the real part (ε_r') and the imaginary part (ε_r''). The real part is a measure of the ability of the dielectrics to store electrical energy. The imaginary part is also called the relative dielectric loss factor, which is associated with the dielectric loss. For common nonmagnetic dielectrics, ε_r'' determines the heating rate under MW radiation. As indicated by Eq. (2), the dielectric loss tangent represents the ratio of the

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https://doi.org/10.1016/j.fuproc.2018.05.028
Received 7 February 2018; Received in revised form 23 May 2018; Accepted 24 May 2018
0378-3820/

imaginary part to the real part, referring to the proportion of power loss to power storage.

The dielectric properties of semi-coke determine the feasibility of MW heating of coal [13,14]. The dielectric properties of semi-coke are influenced by its structure. In the process of MW heating, the structure of semi-coke changes continuously, which leads to the changes of the dielectric properties including both the dielectric loss and MW energy absorption capacity. Therefore, it is important to study the structure and dielectric properties of semi-coke derived from MW pyrolysis of low-rank coal and the mechanism of dielectric loss during this process.

A few of papers reported the changes of semi-coke structure and its dielectric properties. The general viewpoint is that most of the carbon in coal exists in an indefinite form, resulting in a highly disordered internal structure and the characteristic of multi-directionality. However, some of the carbon also combines to form microcrystalline structures, resulting in a short-range ordered state on a micro-scale, which is called turbostratic structure [15,16]. With a change of external conditions, such as the deepening of coalification degree and the increasing of heat-treatment intensity, the crystallite structure of carbon will also develop towards the crystal structure of graphite [17,18]. Russell and co-workers [19,20] previously compared the crystal phase structure between char at 2000 °C and natural graphite. The arrangement of carbon layers in the char was very similar to the arrangement of the crystal layers in graphite. Studies by Xu et al. [21,22] showed that the heating temperature could cause significant changes in char structure and the carbon in the disordered state of coal char gradually became directionally parallel with increasing temperature, and the proportion of ordered carbon structure above 1300 °C increased markedly. The structural change of the char resulted in the enhancement of its dielectric properties. However, the research objects of Russell and Xu were high-temperature chars, and they did not investigate the medium-to-low-temperature semi-cokes (chars). Peng et al. [11] studied the changes of dielectric properties of Eastern high-volatility bituminous coal from West Virginia (USA) during pyrolysis. The dielectric properties of semi-coke increased dramatically when the temperature was higher than 500 °C, and the change tended to be gentle at 750 °C and maintained at a high level, in agreement with the study of Wang et al. [23] It was concluded in this study that the structure of semi-coke had changed dramatically, together with the electrical conductivity, resulting in a change of dielectric loss way, but the experimental data was not available.

Based the results from the literatures reported, the mechanism of dielectric loss of coal char is still not clear. In order to deeply understand the correlation among the structure of semi-coke, its dielectric properties and electrical conductivity properties, MW pyrolysis experiments of two low-rank coals were carried out using an MW tube furnace. Dielectric properties were measured using a vector network analyzer at a frequency of 2450 MHz, and the electrical conductivity was measured using a four-probe resistivity tester. The changes in the crystallite structure of semi-coke were characterized and analyzed by X-ray diffraction (XRD) and Fourier-transform–infrared spectroscopy (FTIR). The mechanism of dielectric loss during microwave pyrolysis was discussed in details. This will provide theoretical basis for MW pyrolysis of low-rank coal.

2. Experiment

2.1. Raw coal

Both HX coal and SL coal are low metamorphic coals. HX coal is long-flame coal and SL coal is brown coal. The proximate analysis and ultimate analysis of both are shown in Table 1.

Table 1
Proximate and ultimate analysis of raw coals.

Sample	Proximate analysis/%				Ultimate analysis/%				
	M_{ad}	A_d	V_{daf}	FC_d	C_{daf}	H_{daf}	N_{daf}	O_{daf}	$S_{t,d}$
HX raw coal	3.66	15.56	38.17	52.21	79.86	4.75	0.94	13.73	1.28
SL raw coal	21.17	13.31	42.96	49.45	74.97	4.42	1.14	18.95	0.49

2.2. Microwave pyrolysis experiment

The MW pyrolysis experimental device is shown in Fig. 1. The main experimental MW oven mainly comprises a power supply, magnetron, high-voltage transformer, inverter, high-voltage rectifier circuit, furnace cavity, and operating system components. The MW frequency is 2450 ± 50 MHz, and the maximum power is 1600 W. Under power excitation, the magnetron continues to produce MW radiation, which passes through waveguide system to couple to the furnace chamber. The diameter of the quartz tube reactor is 60 mm, and the length is 950 mm.

After crushing and sieving, the coal particles less than 6 mm were chosen for experiments. Since the MW penetration depth of the two test coal are 1220 mm and 70 mm respectively, much greater than the experimental coal particle size, the coal particle can be heated from the inside and the outside simultaneously in the range of MW penetration depth. Before the experiment, a 50-g coal sample was placed in the quartz boat and sent to the middle of the quartz tube to ensure the accurate measurement of the center temperature of the coal sample. According to Fig. 1, the experimental system was connected to a 99.7%-pure flow of N_2 as a carrier gas to ensure an oxygen-free environment. According to preliminary experimental results, MW power was selected as 800 W, and MW radiation times were set to 5, 10, 15, 20, 25, 30, and 60 min, respectively, and the temperature was recorded. At the end of the experiment, when the temperature of the furnace was naturally cooled to room temperature, the semi-coke products under different MW radiation time were collected and weighed.

2.3. FTIR analysis

The infrared spectrum analysis method can be used to identify the functional groups of coal surfaces with the advantages of few samples, simple sample processing, fast measurement, and convenient operation. A Fourier transformation infrared spectrometer (IRTracer-100, Shimadzu, Japan) was applied to analyze the functional groups of semi-coke by the KBr method. Samples were dried at 120 °C for 3 h before the test, and mixed with KBr at a ratio 1:400, with blank KBr as a background. The test resolution was 4 cm^{-1}, the cumulative number of scanning times was 45, and the scanning spectrum range was 400–4000 cm^{-1}.

2.4. XRD analysis

At present, XRD has become an effective method to study the microstructure of crystal materials and some amorphous materials. A diffractometer (Ultima IV, Rigaku, Japan) was used to carry out qualitative and quantitative analysis of the phase and crystal structure of the semi-cokes by recording the diffraction of each crystal phase of the sample. Cu $K\alpha$ radiation (40 kV, 40 mA) was used as the X-ray source. The XRD patterns were recorded at a scanning speed of 4°/min, with a step size of 0.02° and a 2θ angular range of 5°–70°.

2.5. Dielectric properties measurement

There are many methods of measuring dielectric properties of dielectric materials. In this paper, the coaxial probe method is used at 2450 MHz, and the test system is shown in Fig. 2.

Before testing, the coal sample was broken and ground to less than 200 meshes in order to reduce the influence of air between coal