Fuel 153 (2015) 249–256

Contents lists available at ScienceDirect

Fuel

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

Effect of coal rank on structure and dielectric properties of chars

Haiyu Liu *, Liang Xu, Yan Jin *, Baoguo Fan, Xiaolei Qiao, Yanxia Yang

School of Electrical and Power Engineering, Taiyuan University of Technology, Taiyuan 030024, PR China

HIGHLIGHTS

- Dielectric properties of coal chars were evidently dependent on coal rank.
- High rank coal chars showed higher values of dielectric constant and loss factor.
- High rank coal chars showed a higher aromatic carbon concentration.
- Carbon stacking and aromatic carbon concentration account for dielectric properties.

ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form 3 March 2015
Accepted 4 March 2015
Available online 16 March 2015

Keywords:
Dielectric property
Coal rank
Carbon crystallite
Aromatic carbon

ABSTRACT

The study was undertaken to investigate the effect of coal rank on dielectric properties, through structural differences of various coal chars. Chars from three different coals were prepared in the temperature range 850–1600 °C, and dielectric properties were determined by a vector network analyzer in the 2–18 GHz frequency range. Crystalline structure of char samples was characterized using X-ray diffraction, and the relative concentration of aromatic structure was further assessed by Fourier transform infrared spectroscopy. Results show that the relative dielectric constant and dielectric loss factor of chars largely depended on coal rank, and carbon layer stacking in combination with aromatic carbon content, related to orientation polarization, could account for dielectric properties of chars from different rank coals. Moreover, a considerable amount of silicon carbide was found in higher temperature chars, which greatly improved microwave dielectric absorption.

1. Introduction

Microwaves lie between ultra-short waves and far-infrared waves within the space electromagnetic spectrum, corresponding to frequencies from 0.3 to 300 GHz. Microwave-related technology has gained increasing applications in many industrial fields over the last decades, since microwave can be acquired simply and regulated easily. Microwave is also recognized as a potential energy for heating and measuring [1–8], which has attracted much interest among researchers and practitioners.

The widely used microwave technique is based on interaction between the material and microwave. When exposed to microwave radiation, a dielectric material often responses to the alternating electromagnetic field through its complex permittivity, as well as simultaneously absorbs the field energy which is transformed into heat generation. The complex permittivity and the absorbed power per unit volume of the present material are defined in Eqs. (1) and (2) [9], respectively.

$$\varepsilon^* = \varepsilon'_r - j\varepsilon''_r \tag{1}$$

$$P = 2\pi f \varepsilon_0 \varepsilon'_r \tan\delta |E|^2 \tag{2}$$

where ε'_r, the real component of complex permittivity ε^*, also called the relative dielectric constant and ε''_r, the imaginary component of complex permittivity, also called the dielectric loss factor, are related to polarization and energy loss, representing coupling ability of material with transmission microwave, j equals $\sqrt{-1}$, E is the electric field magnitude, f is the microwave frequency, ε_0 is the permittivity of free space, $\tan\delta$ is the dielectric loss tangent, referring to the fractional power loss as compared to power storage, which is described as:

$$\tan\delta = \frac{\varepsilon''_r}{\varepsilon'_r} \tag{3}$$

It is clear from the above equations that energy absorption is dominated much by dielectric properties (ε'_r, ε''_r, $\tan\delta$) in any form of microwave application [10–12]. Knowledge about dielectric

* Corresponding authors. Tel.: +86 13466871287 (H. Liu), +86 351 6014598 (Y. Jin).
E-mail addresses: liuhaiyu@tyut.edu.cn (H. Liu), jinyan@tyut.edu.cn (Y. Jin).

http://dx.doi.org/10.1016/j.fuel.2015.03.008
0016-2361/

properties is not only a fundamental aspect for the interaction between material and microwave, but also the key to process control in microwave engineering.

Microwave have been used in coal pyrolysis for tar production or coke making [13–16], during which dielectric loss and microwave absorption capability are found to increase as a result of the release of volatiles and the ordering of carbon structure. Understanding factors affecting microwave heating and structural changes is effective for optimization, which also appears as a main concern by the majority of researchers [14,17]. However, different original coals have been known to exhibit distinctly different behaviors under heat treatment [18–23], and what is more, structural ordering of coal char is found to be strongly dependent on coal rank [24–27]. Takagi et al. [24] believes that a lower-rank coal contains smaller hexagonal carbon layers and a higher ratio of the bridged structure, so a slower heating rate is required for the development of carbon structure compared with higher-rank coal. Emmerich [25] found the coalescence of crystallites differs distinctly from graphitizable carbons to non-graphitizable carbons, as the coalescence for non-graphitizable chars is dominant at higher temperatures, approximately 1150 °C above that for graphitizable chars. In view of the differences of char structure with coal rank under heat treatment, the dependent dielectric loss and microwave behavior are therefore imperative in microwave process and final products. Additionally, microwave irradiation for measuring carbon content in fly ash is based on the dielectric constant and microwave attenuation properties of residual carbon [28–30]. Coal rank, though, has been proved to influence the morphology and physicochemical properties of residual carbon, which may not be ignored for precision microwave measurement. Consequently, it is vital to verify structural differences between chars from different rank coals, and their possible effects on dielectric properties for microwave applications in both heating and measurement, but not much attention is paid in this aspect yet.

The aim of this paper is to achieve a better understanding of the influence of coal rank on microwave dielectric behavior, through reporting the relationship between dielectric properties and structural differences of various coal chars. Char samples were produced from three coals of different rank at 850–1600 °C, and their dielectric properties were examined in the microwave frequency range of 2–18 GHz. Crystal structure was determined by the means of X-ray diffraction (XRD). To facilitate the characterization, Fourier transform infrared (FTIR) spectroscopy technique was further applied for the evolution of functional groups and the assessment of relative content of carbon radicals between chars from different rank coals. At the base of structural parameters obtained from quantitative characterizations, the dependence of dielectric properties on char structure was discussed in detail.

2. Experimental

2.1. Coal acquisition and char preparation

Three coals of different rank were used for this investigation: a brown coal (HE) from Yunnan Province in Southwest China, a bituminous coal (YAN) and an anthracite coal (WU), from Shanxi Province in North China. The proximate and ultimate analyses of these coals are represented in Table 1, and ash analyses are shown in Table 2.

Raw coals were pretreated by crushing, grinding and sieving, and the portion that passed through a 200 mesh sieve was used to produce chars in a horizontal tube reactor, with a precision temperature controller. A stream of nitrogen was drawn into the tube furnace while pulverized coals were feed into the center of the high-temperature furnace, and then chars was prepared in the temperature range between 850 °C and 1600 °C, with an interval of 150 °C. At each setting temperature, coal chars were kept for 10 min, so as to ensure the release of volatile matters and give the time for the development of char structure, especial for those at lower temperatures. To facilitate discussion in this paper, char samples were named after the original coal and generation temperature, so YAN1300 was taken as an example to represent coal char which generated from YAN at 1300 °C.

Table 1
Proximate and ultimate analyses of three raw coals.

Coal	Proximate analysis (%, dry basis)			Ultimate analysis (%, dry basis)				
	Ash	Volatile	Fixed carbon	C	H	N	S	O
HE	17.01	46.31	36.68	58.33	5.27	1.98	2.35	15.06
YAN	12.27	34.45	53.28	71.46	3.96	0.96	0.26	11.09
WU	36.92	8.29	54.79	57.43	1.54	0.85	0.24	3.02

2.2. Measurement of dielectric properties

Dielectric properties (the relative dielectric loss and the relative dielectric factor) of coal chars were assessed at microwave frequency between 2 GHz and 18 GHz, by a measurement apparatus mainly composed of a vector network analyzer (Model N5244A, Agilent, USA). A coaxial test fixture with char samples embedded in paraffin wax was coupled to a coaxial cable, and then the induced signals in the transmission line were detected by the vector network analyzer (VNA), which were further utilized for deducing the relative dielectric constant and dielectric factor using Nicholson–Ross–Weir (NRW) transmission/reflection method. The dielectric loss tangent was calculated from Eq. (3).

And, for the special touch, the mixing ratio of char sample with paraffin wax is a vital ingredient for the comparison of dielectric parameters of chars, due to different mineral contents of raw coals with different ranks. Whereas carbon is often suggested to perform much more dielectric loss and microwave attenuation for the much greater permittivity, relative to mineral matters in chars [28,31,32]. In this paper, the amount of char samples was adjusted to a same carbon level in the coaxial test fixture for each measurement, which was assigned in a 2:3 ratio.

2.3. XRD experiment

Char samples were all subjected to XRD analysis. An X-ray diffractometer (Model XRD-6000, Shimadzu, Japan) with Cu Kα radiation was applied to obtain structural information of fine powder crystals, through sample profiles of X-ray intensity varied with diffraction angle. The XRD patterns were recorded from a start angle $2\theta = 5°$ to an end angle of 65°, with a step size of 0.2° and a scanning speed of $8° \text{ min}^{-1}$. A full-profile analysis software package (Jade v9.0, Materials Data, Inc., USA) was employed for phase identification and quantitative characterization of crystal structure.

2.4. FTIR measurement

Chars from three coals were tested for carbon skeletons and functional groups, by Fourier transform infrared (FTIR) spectroscopy experiment. The mixture of char sample and potassium bromide (KBr) at the ratio of 1:120 was grinded for 10 min in an agate mortar, afterwards molded into a round slice under a pressure of 10 MPa. The disc was then radiated by a FTIR spectrophotometer (Model Vertex 70, Bruker optics, Germany), and absorbance spectra were recorded at a resolution of 2 cm^{-1} in