Fuel 115 (2014) 685–696

Contents lists available at ScienceDirect

Fuel

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

Chemical properties of superfine pulverized coals. Part 2. Demineralization effects on free radical characteristics

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HIGHLIGHTS

- EPR and power saturation techniques were used to study free radical characteristics of acid treated coals.
- Coals with higher maturities, larger coal particles and the acid treated samples are much more easily saturated.
- EPR spectra of acid treated coals are superposition of 1 Gaussian and 3 Lorentzian lines.
- Free radicals remaining in coals during acid washing are determined by a competing mechanism.

ARTICLE INFO

Article history:
Received 27 March 2013
Received in revised form 23 July 2013
Accepted 24 July 2013
Available online 8 August 2013

Keywords:
Superfine pulverized coal particle
Free radical
Electron paramagnetic resonance
Demineralization
Power saturation behavior

ABSTRACT

Inorganic matter in coal significantly influences its chemical properties and potential utilizations. Electron paramagnetic resonance (EPR) characteristics can be affected by inorganic species, and various groups of paramagnetic centers behave differently after demineralization procedures. In this paper, EPR and the power saturation technique were applied to investigate thoroughly the free radical characteristics of acid-treated superfine pulverized coals. Systematic studies were conducted to explore the behaviors of different groups of paramagnetic centers in demineralized and pyrite-free coals. Focus was directed on comparisons of free radical characteristics of coal samples with different particle sizes, indicating that coals with higher maturities and larger particle sizes are much more easily saturated. Compared to raw coals, the acid-treated samples are more susceptible to saturation. Furthermore, the power saturation technique also served as a quantitative analysis method to study the line-broadening mechanism. This technique revealed that the components in coals with higher molecular weights contain more homogeneous components. Worth noticing is that the concentrations of free radicals residues in the acid-treated coals are determined by two competing mechanisms. The oxidation effects would increase the amounts of free radicals while the removal process of certain components in coals has decreasing effects. Multi-component spectra studies reflect that EPR spectra of acid-treated coals are superimposed by one Gaussian and three Lorentzian lines.

1. Introduction

Coal has a complex structure with heterogeneous and variable substances composed of organic and inorganic materials. Coal's inorganic matter has significant influences on its potential utilizations, such as the tar yields, liquid and gaseous products [1,2]. Coal washing techniques, prior to combustion, have been applied to increase coal qualities. These techniques are considered important for environmental protection. In recent years, ultraclean coal techniques, usable in direct coal-fired gas turbines as well as in advanced coal combustion technologies such as pressurized FBC (Fluidized Bed Combustion) and IGCC (Integrated Gasification Combined Cycle), have caused growing concerns [3]. Coal structure and reactivity are likely changed during the chemical demineralization processes, which influence the potential utilizations of coals, necessitating the study of the demineralization effects on coal chemical characteristics.

Ever since Uebersfeld et al. [4] and Ingram et al. [5] discovered an appreciable concentration of stable free radicals in natural carbons, the roles of carbon radicals and the changes of their properties in coals during chemical processes have attracted much attention [6]. It is generally recognized that free radicals play a crucial role in carbonization, gasification, pyrolysis processes and liquefaction reactions. Moreover, radicals can also provide information on certain chemical species in coal [7]. Electron paramagnetic resonance (EPR) as a nondestructive, well-established technique, has been widely used in the study of free radicals in coals [8]. Retcofsky et al. [9] studied the chemistry of a series of coal samples from America by applying the EPR technique,

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http://dx.doi.org/10.1016/j.fuel.2013.07.099

suggesting that free radicals mainly exist in organic structures containing carbon, hydrogen, and oxygen. EPR characteristics of isolated coal macerals were also studied; different groups of paramagnetic centers were detected in separate species [10]. Petrakis and Grandy [11] established the presence, concentration, and nature of free radicals in several coal related samples and summarized the *g*-values of several possible compound types of radicals in coals. They elucidated that free radicals likely play a significant role in coal conversion processes and can offer an excellent method by which to understand coal structures. Hayes and Hadad [12] investigated combustion pathways of the alkylated heteroaromatics using the density functional theory (DFT) methodology. They found that the necessary first step in any combustion pathway is the generation of oxidized radical species. Curtis and Pellegrino [13] suggested the precondition for the coal liquefaction process is the thermal cleavage of relatively weak bonds, i.e. the formation of free radicals. These radicals could then be stabilized in the presence of hydrogen donor solvents, coinciding with other research [14,15].

The above investigations were initiated based on whole coals with the presence of inorganic species. It is known that some of the unpaired electrons on molecules couple magnetically with inorganic matter in coals. Besides the organic free radicals, certain complex compounds with metal ions, especially transition-metal ions, such as Mn^{2+}, Cu^{2+}, Fe^{3+} and Fe^{2+}, have strong effects on the observed free radical properties. Carbon radicals in the organic materials of coals interact with inorganic paramagnetic species that occur in both mineral and ionic forms [16]. Therefore, inorganic species significantly affect EPR characteristics. The behaviors of different groups of paramagnetic centers, alter during demineralization processes. Silbernagel et al. [16] reported EPR observations for coals before and after demineralization, specifically change in radical densities, *g*-values, and linewidths during acid washing processes. Pilawa et al. [17] compared oxidation effects on free radicals in demineralized coals and coals free of pyrite. Three different types of free radicals were detected in coal samples. Demineralization and oxidation processes had different influences on different paramagnetic centers. The proposal of combustion with superfine pulverized coal, the average particle size around or below 20 μm, has provided a new way to understand the effect of particle size on the combustion process. It is accepted that bond breakings occur under intense external forces during the comminution of superfine pulverized coals, producing large amounts of free radicals. Particle sizes significantly influence the radical properties of coals. However, not enough attention has been dedicated in previous studies to the influences of fragmentation on radical properties in the parent coals, not to mention demineralized coal samples. Systematic studies specifically centered on the behaviors of different groups of paramagnetic centers in demineralized and pyrite-free coal samples in this paper. The relationships between coal particle sizes and free radical characteristics comprised the central focus. The *g*-values, lineshapes, linewidths, integrated intensities, and power saturation characteristics of EPR spectra from different kinds of superfine pulverized coals were recorded and analyzed in detail.

2. Materials and methods

2.1. Preparation of raw superfine pulverized coal samples

Shenhua (SH), Nei Monggol (NMG), and Yangquan (YQ) coal samples from different Chinese coalfields with diverse maturities were chosen for the experiments. A QLM-80K fluidized bed jet mill (China) was employed to produce the superfine coal particles. The preparation process was described in our previous work [18]. The particle-size distributions of the particles were analyzed by the Malvern MAM5004 Laser Mastersizer (UK). The resulting equivalent mean particle sizes of YQ samples are 5.38, 17.3, 23.9, and 38.8 μm. The sizes of SH samples are 14.7, 17.4, 21.3, and 44.2 μm while NMG samples are 12.5, 14.9, 25.8, and 52.7 μm. The properties of the coals, i.e. the ultimate and proximate analyses, are listed in Table 1. The ultimate analysis data were obtained on Vario ELIII (Elementar, Germany), and the oxygen content was obtained by difference. The proximate analyses were implemented on LECO MAC 500 (America), which infers that both SH and NMG coal samples are bituminous coals while YQ coal samples belong to anthracite. X-ray fluorescence (XRF) was applied to analyze the ash compositions of SH and NMG coals, listed in the *Supplementary* Table S1. A method for the direct determination of certain oxides in coal ashes collected at 815 °C by normal XRF with powder pellets preparation was adopted. It can be observed that there is a large proportion of transition-metal components, such as Fe and Ti, that might introduce paramagnetic center signals to coal particles. There are other transition-metal elements which can interfere with the free radical properties in raw coals. The hard X-ray micro-focus beamline (BL15U1) at Shanghai Synchrotron Radiation Facility (SSRF) was applied to study the elemental, chemical, and structural information of raw superfine pulverized coals. We analyzed the results of micro-focus X-ray fluorescence (μ-XRF) and imaging focused on single raw coal particles. Typical μ-SRXRF spectra scanned from single particles of raw SH and NMG coals are shown in the *Supplementary* Figs. S1 and S2, which can provide the elemental information of coal particles. Elements distribution within single coal particles is reflected in the *Supplementary* Figs. S3 and S4. The results prove that there are many transition-metal elements, such as Fe, Mn, and Co, distributed similarly in coal particles that might occur in both mineral and ionic forms. Carbon radicals in the organic materials of coals that interact with these species must influence free radical properties in specific ways. Therefore, demineralization procedures were adopted here to study the effects of inorganic matter on coal free radical properties.

2.2. Preparation of demineralized and pyrite-free coal samples

To study the effects of inorganic matter on the free radical properties, demineralized and pyrite-free coal samples were prepared from raw coals, following the procedures of the Chinese Standard (GB/T 7560-2001). The HCl/HF demineralization procedure was implemented to obtain demineralized coal samples, during which most coal mineral matter, such as clay, carbonate, and silicate are removed. The main residual mineral constituents are crystal-

Table 1
Ultimate and proximate analysis of tested coal samples.

Proximate analysis (wt%) (ad)		Ultimate analysis (wt%) (ad)	
SH			
Moisture (mass%)	11.5	C	63.13
Volatile (mass%)	24.22	H	3.62
Ash (mass%)	10.7	O	9.94
Fixed carbon (mass%)	53.58	N	0.70
		S	0.41
NMG			
Moisture (mass%)	14.72	C	54.82
Volatile (mass%)	35.69	H	4.39
Ash (mass%)	10.64	O	14.58
Fixed carbon (mass%)	38.95	N	0.63
		S	0.22
YQ			
Moisture (mass%)	1.06	C	79.07
Volatile (mass%)	7.98	H	3.47
Ash (mass%)	12.43	O	1.01
Fixed carbon (mass%)	78.53	N	1.14
		S	1.82