Powder Technology 272 (2015) 64–74

Contents lists available at ScienceDirect

Powder Technology

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

Influences of particle size, ultraviolet irradiation and pyrolysis temperature on stable free radicals in coal

Jiaxun Liu, Xiumin Jiang *, Jun Shen, Hai Zhang

School of Mechanical Engineering, Shanghai Jiao Tong University, Minhang District, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form 6 November 2014
Accepted 9 November 2014
Available online 15 November 2014

Keywords:
Pulverized coal
Free radical
Super-fine comminution
Pyrolysis
Ultraviolet irradiation

ABSTRACT

Free radicals play an important part in coal utilization, such as carbonization, gasification, liquefaction and pyrolysis processes. The diagenesis of organic sediment, pyrolytic reactions during metamorphosis and radiolysis are the three possible geneses of stable free radicals in coal. The influences of different origins on the nature of free radicals and their subsequent behaviors during the coal utilization are of great interest. In this paper, three experimental studies of super-fine comminution, fixed-bed pyrolysis and in situ ultraviolet irradiation were adopted to investigate the behaviors of the paramagnetic centers in coal/char. The nature of different radical species in coal/char during the influential processes was focused through the deconvolution study of the electron paramagnetic resonance (EPR) spectra. Final results indicate that the comminution, pyrolysis and ultraviolet (UV) irradiation are all effective ways to initiate the free radicals. The super-fine comminution has noticeable influence on the aromatic hydrocarbon radicals. The UV irradiation can promote the formation of the σ-type oxygen-containing radicals in coal. Furthermore, the simple aromatic clusters and the σ-type oxygen-containing radicals are the most active types during thermal degradation of pulverized coal particles.

1. Introduction

Ever since Uebersfeld et al. [1] and Ingram et al. [2] discovered the electron spin resonance absorption in natural carbons, a non-destructive technique of electron paramagnetic resonance (EPR) has been widely adopted to investigate coal and carbon materials [3–5]. Hayes and Hadad [6] pointed out that during any combustion process, the generation of radical species that could be subsequently oxidized may be a necessary first step. Additionally, the formation of free radicals as the precondition plays a key role during coal liquefaction processes [7,8]. More importantly, the nitrogen evolution is believed to be related to the free radical attack on nitrogen heteroatoms [9]. Chang et al. [10] claimed that the formation of precursors such as NH_3 and HCN is tremendously affected by the donable hydrogen (i.e., availability of H radicals). Above all, it is widely accepted that the free radicals play an important part in coal utilization activities like carbonization, volatilization, liquefaction, pyrolysis and gasification [11–13].

There are three possible geneses of stable free radicals in coal: radicals that have persisted through the diagenesis of the organic sediment, radicals that were formed in pyrolytic reactions during metamorphosis, and radicals that were produced by radiolysis [14]. Then, it will be interesting to find out the influence of these different origins on the nature of free radicals and their subsequent behaviors during the coal utilization. Three experimental processes of super-fine comminution, fixed-bed pyrolysis and ultraviolet irradiation were adopted to simulate the natural geneses, as depicted in Fig. 1. Mechanochemical effects occur during the super-fine comminution process of pulverized coal. Dalal et al. [15] found that the breakage of coal during grinding processes generated free radicals in coal. The fragmentation process is a key factor of producing and initiating free radical reactions. Additionally, the free radical reactions are supposed to happen during the coal pyrolysis process. When coal is heated, the homolysis of covalent bonds is susceptible to occur, which presumably promotes the formations of free radicals. Qiu et al. [16] compared the geological samples and the thermal simulated coal, and pointed out that the radical concentration was maturity dependent. The low temperature weathering processes of coal were investigated by Green et al. [17]. The results showed that the oxidation mechanisms involved radical reactions on the coal surfaces. The lower rank coals were more susceptible to the oxygen-derived radicals. Zhan et al. [18] investigated the thermal decomposition process of subbituminous coal applying ReaxFF MD (reactive force field, molecular dynamics) simulation. The intramolecular changes involving bond cleavages and radical combination played a key role in the formation of typical pyrolysis products. Li et al. [19] and Zhang et al. [20] adopted similar methods to analyze the catalytic effects of metal species on the pyrolysis of lignite. The final results indicated that metal species accelerated the pyrolysis via decreasing the bond dissociation energy and changing the pathways of cleavage reactions. On the other hand, photolysis can also lead to the formation of radicals. Evans [21] proved the aromatic polymer lignin could strongly absorb ultraviolet (UV) irradiation and produced aromatic and other radicals. Friedel and Breger [22] exposed coals to the pile-irradiation and

* Corresponding author. Tel.: +86 21 34205681; fax: +86 21 34205521.
E-mail address: xiuminjiang@sjtu.edu.cn (X. Jiang).

http://dx.doi.org/10.1016/j.powtec.2014.11.017
0032-5910/

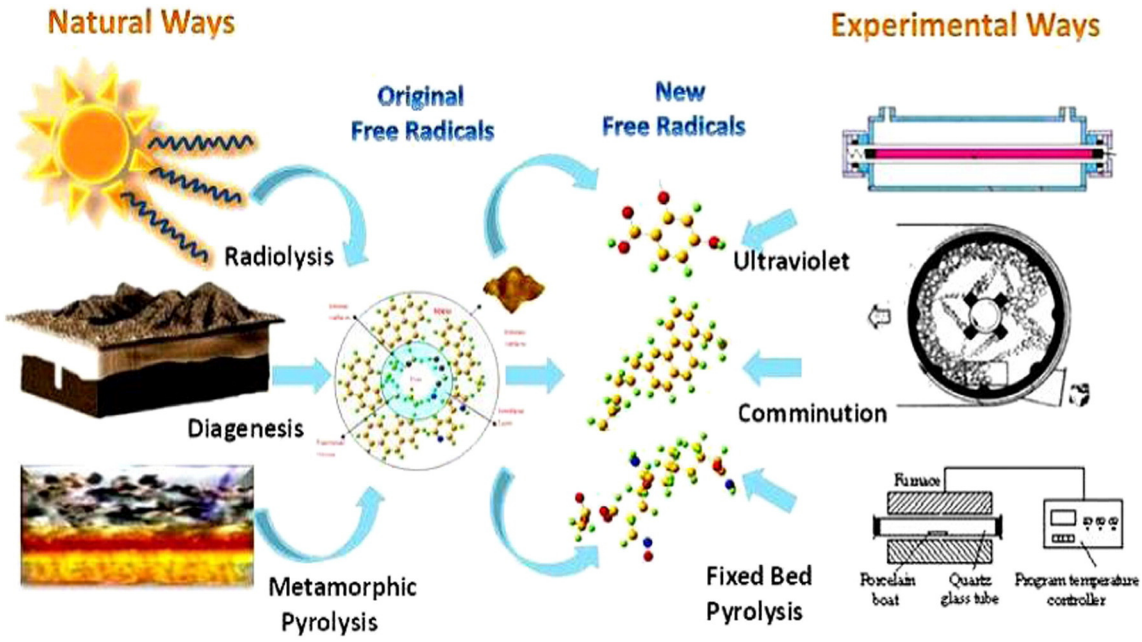

Fig. 1. Different ways for the genesis of free radicals in coal.

found the two coals with highest carbon content had a notable growth in free radicals. The photodissociation mechanisms of aromatic molecules are complicated, which involve multiple dynamical channels [23]. The photochemical dissociation of covalent bonds may be attributed to the high vibrational excited state of the ground state or triplet state, which produces hot molecular radicals [24]. Besides, the effect of substitution may also play an important role in the photodissociation dynamics, which influences the inductive, steric, and conjugation properties of the molecular system [25].

Therefore, comminution, pyrolysis and UV irradiation are three effective ways to initiate the free radicals in coal. The overall EPR spectrum of coal is an envelope curve that is superimposed of the spectra reflecting all the paramagnetic components [26]. The overlapped lines are attributed to the diverse paramagnetic centers located on different molecular structures of coal. However, the roles of individual groups of free radicals in different chemical processes are not well known so far. Few studies focused on the influence of fragmentation and UV irradiation on free radicals in pulverized coal. The behaviors and properties of specific groups of free radicals during different influential processes are not fully understood yet.

In this paper, the deconvolution of the EPR spectra was conducted through numerical analysis, applying computer techniques. The individual component lines in the multi-component EPR spectra were recorded. The influences of particle size, ultraviolet irradiation and temperature on different types of free radicals in coal were studied thoroughly.

2. Experimental section

Two kinds of coal with the distinct qualities, Shenhua (SH) and Nei Monggol (NMG) coals, were selected in this work, which were comminuted into different particle sizes. The equivalent mean particle sizes of NMG coal are 12.5, 14.9, 25.8 and 52.7 μm, while that of SH samples are 14.7, 17.4, 21.3 and 44.2 μm. The properties of the coal samples were discussed substantially elsewhere [13,14] and listed in Table S1 in the supplementary material for a reference. Both NMG and SH coal samples belong to medium volatile bituminous coals. The coalification degree of NMG coals is lower, which have a higher reactivity compared to SH coals. During the coalification process, the concentrations of oxygenated functionalities such as methoxy groups decrease with the increase of coal rank, which causes the lower oxygen content of SH coals. While the unpaired electrons associated with large aromatic ring structures are stabilized with the increase of aromaticity and carbon content. Thus, there are more stable aromatic species and less active oxygen-derived free radicals in SH coals. Therefore, NMG coals with higher volatile content are of stronger cokeability and activity. Furthermore, the petrographic characteristics might also influence the reactivity of coals, which is also summarized in Table S1. Better caking properties of NMG coals can be expected due to the higher content of vitrinite.

Our previous study [27] shows the EPR characteristics are affected significantly by inorganic species because of the unpaired electrons that coupled with inorganic matter magnetically in coal. Additionally, transition metal ions such as Fe^{2+}, Cu^{2+} and Mn^{2+} in the complex disturb the observation of free radicals. Therefore, acid washed coal samples were used in all the experiments. The pyrite-free coal particles were obtained through the acid treatment. The detailed demineralization procedures can be found in our previous works [27,28]. A fixed-bed reactor was applied to perform the coal pyrolysis experiments [28]. The chars were created in the highly purified N_2 (99.999%) or CO_2 (99.999%) atmosphere. The coal samples (about 0.4 g, placed in a porcelain boat) were heated up in a furnace adjusted by a temperature controller. The flow rate of the carrier gas was regulated to 3 L/min by a mass flow controller.

EPR experiments were performed in a Brucker EMX-8 spectrometer (Germany, X-band, frequency 9.87 GHz, modulation 100 kHz), operating at the ambient temperature. The attenuation of 40 dB was adopted to avoid the signal saturation. The detailed operating parameters of EPR spectrometer were depicted before [28]. 2,2-diphenyl-1-picryhydrazyl (DPPH, $g = 2.0036$) was adopted as the reference for the quantification of radical concentrations. A measured amount of the sample was placed into a 2 mm quartz EPR tube immediately after the experimental operations (i.e., comminution, pyrolysis and UV irradiation). The tubes were filled with argon gas and then sealed.

A 1 kW, high-pressure, mercury arc lamp was utilized for the ultraviolet irradiation. The lamp has intense emissions in the ultraviolet region (365–366 nm), and the UV irradiation intensity is 1000–9500 MJ/cm^2. The distance from the lamp to the sample was fixed to 200 mm in all the photolysis experiments.