



Influences of ultrafine comminution on chemical properties of antibiotic bioferment residue



Zhiqiang Wang¹, Chen Hong^{*,1}, Yi Xing^{*}, Lihui Feng, Yifei Li, Mengmeng Jia

Department of Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:

Received 28 March 2017

Received in revised form 25 July 2017

Accepted 2 August 2017

Available online 5 August 2017

Keywords:

Antibiotic bioferment residue

Ultrafine comminution

Carbon structures

Free radicals

Deconvolution of multi-component spectra

ABSTRACT

The influence of mechanochemical effects on chemical properties of antibiotic bioferment residue (ABR) during the comminution process was studied. The solid-state ¹³C nuclear magnetic resonance (NMR) and electron spin resonance (ESR) techniques were used to study the carbon structures and free radical characteristics of ultrafine ABR. Results showed that with the decrease of particle sizes, the net-like macromolecular aliphatic structures were cracked into numerous short-chain aliphatic carbons, leading to the increase of methylene and methine groups. The side chains of methoxy and oxygen-bonded methine groups initiated the bond cleavage and turned into oxygen-bonded methylene groups. In addition, the degree of aromatization of ABR increased during the grinding process due to the generation of more aromatic structures and the condensation among the aromatic rings. ESR spectra of ABR were the sum of several absorption lines caused different paramagnetic centers, which could be fitted by two Gaussian curves and one Lorenz curve. The effects of particle sizes on g-values, radical concentrations, and linewidths were analyzed. Results indicated that during the ultrafine pulverizing process, mechanical forces induced the cleavage of chemical bonds because of the severe collisions between the ABR particles, thereby producing more free radicals. The concentration of free radicals rose from 1.891×10^{18} to 2.255×10^{18} spin/g. In addition, more reactive sites generated with the increase of the free radicals in ABR, which was conducive to the chemical adsorption of NO_x and its reduction into N₂ in combustion reactions.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Antibiotic bioferment residue (ABR), an organic waste from the antibiotic production, is mainly consisted of mycelia, surplus components of culture media, intermediate metabolites, a small quantity of residual antibiotics [1]. These constituents lead to very high quantities of proteins, fats, and polysaccharides in ABR [2,3]. China is the world's largest producer and consumer of antibiotics, and 80% of cephalosporin, 75% of penicillin, and 90% of streptomycin are sourced from China. The residual antibiotics in the dreg are easy to accumulate and may build up antibiotic resistance in organisms. In fact, ABR was listed in the *National Catalogue of Hazardous Wastes* (HW 02) in 2008.

Burned or used as an auxiliary fuel is an effective way to realize harmless disposal and resource recovery of ABR. Jiang et al. [4] investigated the pyrolysis/combustion behaviors of ABR using TG-FTIR analysis and performed the industrial test of co-combustion of ABR with municipal solid waste (MSW) and coal. These authors concluded that the addition of ABR to MSW/coal did not significantly affect the

incineration system performance or pollutant emissions. Du et al. [5,6] studied the co-combustion behavior of ABR and coal, analyzed the chemical reaction characteristics at different combustion stages, and found that a synergistic reaction might occur between the two at high temperatures. In the combustion process, the particle size might greatly affect the heat transfer efficiency and interface chemical reaction of the fuel. This is mainly because mechanochemical effects can appreciably change the chemical properties of materials during the comminution process. Mechanical forces generally exert on materials in the form of shear, friction, impact, extrusion stress, leading to elastic deformation, lattice defects, plastic deformation and structural failure [7–10]. These changes facilitate chemical reactions on the material surface, such as the cleavage and formation of chemical bonds and the production and coupling of free radicals.

Liu et al. [11] discovered that during the grinding process, the extrusion stress and shear stress changed the chemical structures of coal, enhancing the degree of aromatization of coal. In addition, some large multi-ring aromatic structures in coal under mechanical forces converted into simple aromatic fragments. Guerra et al. [12] observed that the grinding process could affect the chemical structures of lignin; with higher grinding intensity, more alkyl ether bonds might be ruptured, and the contents of carboxylic acid and phenolic hydroxyl groups increased.

* Corresponding authors at: Beijing Key Laboratory of Resource-oriented Treatment of Industrial Pollutants, University of Science and Technology Beijing, Beijing 100083, China.

E-mail addresses: hongchen@ustb.edu.cn (C. Hong), xingyi@ustb.edu.cn (Y. Xing).

¹ These authors contributed equally to this work.

Free radicals are atoms or groups containing unpaired electrons and form by the homolysis of covalent bonds. The lifetime of free radicals has very large difference, and some radicals with short lifespans last for only nanoseconds and are very difficult to detect [13]. By contrast, detectable free radicals generally are long-lived and stable due to the poor steric hindrance mobility or inaccessibility [14]. Electron spin resonance (ESR) technique has been widely applied in the study of free radical properties, and many studies indicated that fossil fuels and biomass contain large amounts of stable free radicals [15–18]. He et al. [16] measured the ESR spectra parameters of walnut shell and corncob, and found that the radical intensity reached a level of 10^{16} spins/g. Wang et al. [18] analyzed the properties of free radicals in oil shale after pyrolysis and discovered that the free radical concentrations increased with the increasing pyrolysis temperature. Furthermore, mechanochemical effects can significantly affect the properties of free radicals. Liu et al. [15] studied the impacts of treatment conditions on stable free radicals in coal and measured the intensity, g -values, and linewidths of ESR spectra. Results indicated that the free radical concentrations of superfine pulverized coal increased sharply during the process of fragmentation. Wei et al. [19] also confirmed that grinding was a key factor in initiating free radicals reactions and markedly increased the contents of active free radicals in coal. Datal et al. [20] observed that anthracite could produce more free radicals during grinding compared with lignite.

Thus far, many studies have focused on the chemical properties of ultrafine pulverized coal particles. However, the variations in the chemical properties of ABR as a potential biomass fuel during the comminution process have been rarely reported. In this paper, ^{13}C solid-state nuclear magnetic resonance (NMR) was adopted to explore the carbon structures of ultrafine ABR particles. The free radical characteristics in ABR (including g -values, radical concentrations, and linewidths) were systematically studied by analyzing ESR spectra. ABR has a number of paramagnetic centers due to its complex structures. ESR spectra are the superposition of several lines induced by different paramagnetic centers. However, the variations of different groups of free radicals in the grinding process are not also well known. Therefore, the individual components of multi-component structures in ABR were investigated thoroughly through the deconvolution of the ESR spectra.

2. Material and methods

2.1. Material and sample preparation

The antibiotic bioferment residue (ABR) used for this study was sampled from a terramycin production process in a medical factory located in Hebei Province, China. The proximate and ultimate analysis of ABR, obtained from TGA2000 (Navas, America) and Vario EL cube (Elementar, Germany), respectively, are shown in Table 1. Before the experiments, ABR sample was dried to a constant weight in a DGH-9023A electrothermal blast drying oven (Pinggang, China) at $105\text{ }^\circ\text{C}$, and pulverized into different mean particle sizes using a QLM-90K fluidized bed jet mill (China). The size distribution of the particles was analyzed by a Mastersizer3000 laser particle-size analyzer (Malvern, U.K.). The sizes of ABR samples are 11.02, 16.38, 24.43, 33.19, and $46.68\text{ }\mu\text{m}$, respectively, and its particle size distribution is presented in Fig. 1.

Table 1

The proximate and ultimate analysis of tested ABR samples.

Proximate analysis (wt%)		Ultimate analysis (wt%)	
Moisture	2.57	C	44.54
Volatile	64.82	H	4.76
Ash	12.16	O	26.91
Fixed carbon	20.45	N	8.42
		S	0.64

Nitrogen adsorption and desorption isotherms of ABR samples were taken at 77 K using a Tristar II 3020 surface area analyzer (Micromeritics, US). The Brunauer–Emmett–Teller (BET) method and Barrett–Johner–Halendar (BJH) method were used to analyze the specific surface areas (S_{BET}) and total pore volume (V_{T}) in the mesoporous range, respectively. As shown in Table 2, the BET surface and total pore volume of ABR samples gradually increased with the decrease of particle sizes, whereas the mean pore diameter showed the opposite trend, which may be ascribed to the exposure of more closed pores.

2.2. ^{13}C NMR spectroscopy

The ^{13}C solid-state NMR spectroscopy has been widely used in non-destructive studies of the carbon skeletal structures of fossil fuels. The development of the cross polarization/magic angle spinning (CP/MAS) technique greatly facilitated NMR applications to solid fuels because it can improve signal-to-noise ratios [21]. Meanwhile, spinning sidebands can be removed by the use of total sideband suppression (TOSS) technique. In this study, the ^{13}C solid-state CP/MAS/TOSS NMR spectroscopy was used to determine the carbon structural features of ABR. All experimental spectra were acquired on an Advance 400 MHz NMR spectrometer (Bruker, Germany), operating at a frequency of 100.63 MHz and spinning speed of 5 kHz. The contact time and pulse repetition delay of ^{13}C – ^1H CP/MAS experiments were 1 ms and 4 s, respectively.

2.3. ESR measurements

The ESR spectroscopy analysis was used to investigate the free radical characteristics of ABR samples. All the experiments were carried out on a JES-FA 200 spectrometer (JEOL, Japan) with an operating frequency of 9.40 GHz. The acquisition parameters during the experiments were as follows: modulation frequency, 100 kHz, X-band; modulation amplitude, 100 Hz; microwave frequency, about 9.07 GHz; microwave power, 0.0997 mW; central magnetic field, 324.254 mT; sweep width, 10 mT; time constant, 0.1 s; sweep time, 60 s. All the observations were accomplished at room temperature and ambient pressure. The deconvolution of the multi-component ESR spectra was carried out through the numerical method using PeakFit software.

The g -values and linewidths (ΔH) were obtained by analyzing ESR spectra with the JEOL computer software CW-ESR. The free radical concentrations reflecting the contents of paramagnetic centers were quantified using a standard curve of 1,1-diphenyl-2-picrylhydrazyl (DPPH) as the reference [11]. The radical concentrations of DPPH (N_d , spins/g) were obtained by the following equation:

$$N_d = \frac{m_d \times 6.02 \times 10^{23}}{M_d} \quad (1)$$

where m_d represents the mass of standard reference DPPH, and M_d represents the molecular mass of DPPH (394.32 g/mol). Meanwhile, the ESR spectra of standard reference DPPH are shown in Fig. S1, and the fitted relationship between A_d and N_d could be described as:

$$A_d = 1834.05N_d \times 10^{-15} - 400.01 \quad (2)$$

The radical concentrations of ultrafine ABR (N_g , spins/g) were calculated by Eq. (3):

$$N_g = \frac{A_g \times N_d}{A_d \times m_g} \quad (3)$$

where m_g represents the mass of the tested ABR samples, and A_g and A_d represent the area under the absorption curves of the sample and DPPH, respectively.

Download English Version:

<https://daneshyari.com/en/article/4914833>

Download Persian Version:

<https://daneshyari.com/article/4914833>

[Daneshyari.com](https://daneshyari.com)