



Influence of critical moisture content in lignite dried by two methods on its physicochemical properties during oxidation at low temperature



Yuhuan Li^a, Hongyu Zhao^{b,*}, Qiang Song^c, Xiaohua Wang^c, Xinqian Shu^c

^a College of Energy and Power Engineering, Inner Mongolia University of Technology, Hohhot 010000, PR China

^b School of Civil and Resource Engineering, University of Science & Technology Beijing, Beijing 100083, PR China

^c School of Chemical and Environmental Engineering, China University of Mining & Technology (Beijing), Beijing 100083, PR China

ARTICLE INFO

Keywords:

Lignite drying
Critical moisture content
Free radical
Low temperature oxidation
Heat release intensity
Pore structure

ABSTRACT

Different drying methods resulted in the pore structure and free radical distribution changing in lignite, and significantly influences its chemical properties and potential utilizations. In this study, the influence of moisture content on characteristic temperature of lignite dried in N₂ and air were explored in a simulating coal oxidation device. Electron Spin Resonance (ESR) and carbon-13 nuclear magnetic resonance (¹³C NMR) were applied to investigate the free radical parameters and the functional groups concentrations in dried lignite. The initial oxidation of lignite occurs at above separation point temperature (SPT), and make pre-dried lignite achieve self-heating. Compared to vacuum drying, the lignite dried in N₂ with critical moisture content of about 15% release more heat during oxidation. Focus was directed on comparisons of free radical characteristics of lignite dried in N₂ at different oxidation temperature, indicating that dried lignite with higher oxidation temperature have a greater free radical concentration and line-width. Mesopore formed by the shrinkage of macropore in lignite dried in N₂ occurred further shrinkage and collapse to form more micropore. When the coal seam temperature reached 140 °C and close to SPT, the yields of gas products such as CO₂ and CO increase rapidly. The values of oxygen-containing functional group measured in FTIR and ¹³C NMR spectra show that the distinct structural feature of lignite dried in vacuum is larger than that of in N₂ due to the greater drying intensity.

1. Introduction

Low-rank coals, i.e. lignites, are considered as the main energy source, which constitute significant supplies for both energy and chemical feedstock, mainly because they represent the most abundant and cheapest fossil fuel available [1–2]. The moisture content of lignite, however, is generally in 25–65%, which leads to lower calorific value, high combustion cost, low energy utilization efficiency and high transportation cost. Drying prior to transportation or use, as the first and essential step in most utilization processes including pyrolysis, gasification and combustion, can improve the calorific value of lignite, utilization efficiency of downstream device and competitiveness in the energy market, and decrease transportation cost [3–4]. Particularly in dehydrated lignite stored in open-air fields [5–7], however, is extremely reactive with oxygen in air at ambient temperature, which involves exothermic reactions between reactive sites in the coal and oxygen, as well as the enhancing or moderating effects that water has on these reactions [8–9]. Actually before spontaneous combustion, the moisture in coal is highly responsive to self-heating due to the low-temperature oxidation [3]. Moreover, the spontaneous combustion of

different coal samples, such as raw lignite, lignite dried in different degrees and chemically treated lignite were closely related to the proportion of micropore, mesopore and macropore and the moisture content in experimental lignite [10–11]. Based upon the previous experimental results, the pore structure was prone to shrink and fracture when the moisture was removed. Therefore, many fundamental researches have been carried out to evaluate accurately the factors that affected the physical and chemical structure of dried lignite in the process of weak oxidation at low temperature [12–15]. However, little information available could be applied to the case of dried lignite considering that characteristic differences emphasized the drying process is synchronous with the structural change of lignite.

It is generally accepted that moisture retained in lignite can be divided into two major forms (i.e., freezable and non-freezable water) on the basis of the characteristic phase transition, which includes conglomeration and fusion [16]. Numerous coal cleaning technologies based on evaporative or non-evaporative methods have been developed to dry lignite and sustainably utilize these dried lignite. It is essential to understand fully of physical and chemical characteristics of dried lignite structure, especially in relation to the dynamical interactions of

* Corresponding author.

E-mail address: yuyu_3003@126.com (H. Zhao).

Nomenclature

M_t	the moisture content of lignite at t moment
W_0	the initial mass of lignite
M_0	the initial moisture content of the lignite
W_t	the mass of lignite at t time
h	planck constant
ν	microwave frequency
μ_B	Bohr magneton
B_r	resonance magnetic field

Abbreviations

SPT	Separation point temperature
-----	------------------------------

CPT	Crossing point temperature
ESR	Electron Paramagnetic Resonance
FTIR	Fourier transform infrared spectroscopy
^{13}C NMR	Nuclear Magnetic Resonance Spectroscopy
XPS	X-ray photoelectron spectroscopy
GC	gas chromatograph
BET	Brunauer-Emmett-Teller
$q_{\max}(T)$	larger than the actual heat release intensity
$q_{\min}(T)$	less than the actual heat release intensity
$V_{\text{CO}}^0(T)$	CO yield at standard oxygen concentration
$V_{\text{CO}_2}^0(T)$	CO ₂ yield at standard oxygen concentration
$V_0(T)$	oxygen consumption rate of coal samples in fresh air
q_a	heat released by chemisorption

moisture content and lignite structure to investigate pore evolution, free radical distribution and functional groups concentration that are fundamental for the subsequent process of thermal conversion and utilization, including combustion and moisture re-adsorption and so on [17–19].

Due to the complicated evolution of the state of moisture transfer in coal and the pore structure, different aspects including coal structure changes during dewatering [20], the forms of moisture present in lignite [8,21], effect of particle size on removal of moisture [10], physical–chemical structure of coal [22–23] and migration path of moisture during dewatering [24] were extensively investigated. Typical characterization techniques and data processing method such as TG-DSC [25], FTIR [26], NMR [27], SEM [28] and curve fitting [29] in measurement and quantification of several properties of practical significance, including types of moisture, carbon and covalent bond cleavage, distribution of functional groups and surface structures of coal sample were also conducted. It should be pointed out that the study about the effect of coal sample structure changes during drying process on self-heating in weak oxidation at low temperature also has important academic and practical significances for preventing spontaneous combustion of lignite. The self-heating of lignite during drying is influenced by many factors, such as moisture content, pore structure and distribution of oxygen-containing functional groups, free radical concentration and so on. Among them, the drying atmosphere and temperature are largely responsible for initiating self-heating and determining the extent to which it develops [8].

Studies on drying temperature, particle size, physical and chemical structure and moisture content of lignite which was thermally upgraded at low temperature using a thermal analysis method are important for measurement of the separation point temperature (SPT) and crossing point temperature (CPT) in the process of self-heating. Zhang et al. [30] using experimental comparison results, found the specific surface area of coal particles gradually increased as the temperature increased, while the average pore size decreased gradually, but the variation range was smaller at the range of 200–400 °C. By means of research about the influence of particle size and moisture in coal at the low temperature oxidation on the spontaneous combustion, Küçük et al. [10] found that the amounts of oxygen functional groups in moist coal samples do not differ significantly compared with that of untreated coal. The liability of spontaneous combustion of treated lignite increased with decreasing particle size, increasing moisture content in coal and decreasing humidity of the air. Furthermore, the particle sizes significantly influence the radical properties of coals. This was demonstrated in a number of studies that the large amounts of free radicals was produced by bond breakings occurred under intense external forces during the comminution of pulverized coals [31].

Herein, much work so far has focused on [32–35] oxygen-containing groups on the surface of coal sample, especially carboxyl and hydroxyl groups which play important roles in the moisture re-

adsorption of dried lignite. This is mainly due to the fact that these groups has a very close relationship with water molecules under the influence of hydrogen-bond interaction [35], they are removed with a great extent in the process of drying due to the moisture re-adsorption rapidly decreased. Similar results were also obtained that pores collapse and lignite shrank as moisture is removed in the process of lignite upgrading. It is worthy to mention that a number of conclusions were obtained in studies that free radicals mainly exist in organic structures containing oxygen, hydrogen, and carbon [31,36]. Petrakis and Grandy [31,37] 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. There are, however, some major limitations in the existing research. Most research that aims to investigate the effect of pretreatment of low rank coal before pyrolysis, gasification and combustion on coal structure, mainly focuses on the comparative experiment of the coal with different metamorphic grade. It is necessary to regard drying as the basis for and necessity of the thermal conversion process [38], especially for physicochemical characteristics of treated coal sample, which would have an important impact on the subsequent applications.

Nevertheless, for conventional description of changes in physicochemical characteristics of lignite dried by the different drying devices during the weak oxidation at low temperature, a number of qualitative analysis have been published yet for the correlation of the changes in physical and chemical structure dried lignite with the different moisture content, which may be propitious to analyse dynamical change along with the moisture content decreased in coal samples. Therefore, as mentioned above, several problematic disadvantages cannot be overlooked, and it is considerably necessary to profoundly understand and reveal the evolution mechanism of moisture content and physicochemical characteristics during weak oxidation in the process of lignite drying, and to investigate the relationship of moisture content and pore structure, oxygen functional groups, heat release intensity and free radical during lignite drying.

Therefore, with the aim to solve the problems mentioned above, there are some significant innovation in this paper. Firstly, the effect of critical moisture content on the heat release intensity and oxygen uptake in coal samples was observed. Secondly, we further discussed the parameters related to free radical concentration of dried lignite at different drying temperatures and medium. And thirdly, the evolution of gas product and the distribution of carbon functionalities functional groups determined by ^{13}C NMR and chemical method were compared. To gain more insight, a comprehensive analytical approach is adopted for the self-heating of pre-dried samples during low-temperature oxidation in a simulating coal oxidation device. It should be pointed out that bond breakings occur under intense external forces during the crush of coals with difference particle size, producing large amounts of

Download English Version:

<https://daneshyari.com/en/article/6473388>

Download Persian Version:

<https://daneshyari.com/article/6473388>

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