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Correlations of chemical properties of high-alkali solid fuels: A comparative study between Zhundong coal and biomass

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ABSTRACT

The utilization of Zhundong coal has given rise to serious ash-related issues mainly because of its high-alkali characteristic, partly similar to biomass with high-potassium content. The chemical properties of such coals and biomass may have marked impacts on reactivity and ash fouling. However, the correlations of different chemical properties of high-alkali solid fuels have been seldom investigated, and then only on a few samples. Here, a comparative study of chemical properties of Zhundong coal and biomass was conducted based on a large database. Correlations between carbon content and ash yield and carbon content and fixed carbon were noted. The fuel ratios of nearly all types of agricultural biomass lay within a range of 0.15–0.30, approximately an order of magnitude lower than those of Zhundong coals, much lower than those of Zhundong coals. There were no significant associations between chemical property and wheat-growing region. In most cases, the ash composition, even for a single biomass type, showed considerable variation, with the K_2O content of wheat and corn straw ash being particularly variable. Most Zhundong coals had medium and similar ash fusion temperatures regardless of the changing ash compositions. Contrary to biomass, the Na_2O content in Zhundong coal ash was an order of magnitude higher than K_2O content. The ash composition of a particular biomass type usually fell in a small region of the ternary diagram of acidic-alkali metal-alkaline earth metal oxide components.

1. Introduction

Coal has an indispensable contribution to chemical industry and electricity generation worldwide [1–5], which has been on large-scale utilized in many countries. Coal is the principal traditional energy in current China and will still occupy a dominant position in the next decades. Zhundong coalfield is one super-huge coalfield newly discovered in Junggar Basin in Xinjiang Autonomous Region of China, with an estimated reserve amount of $\sim 1.64 \times 10^{11}$ ton [6–8]. Because of the super-huge reserve, low exploitation cost and high quality, Zhundong coal will play an ever-increasing role in energy production and chemical industry of China in the near future [8–12]. However, the utilization of Zhundong coal in power plants has brought about serious slagging and fouling problems mainly due to its high-alkali property [13–18]. On the other hand, biomass, a CO_2-neutral and sufficiently "green" renewable solid fuel, has also attracted increasing attention worldwide recently and is a potential alternative to traditional fossil fuels due to the worsening energy crisis and environmental issues. By replacing coal with biomass, the net CO_2 emission per unit heating value could be reduced by 93% [19]. The application of biomass in power generation is rising and the installed capacity of biomass power is expected to rise to 30 GW by 2020 in China [20]. Nevertheless, many issues hinder the safe and efficient utilization of biomass on large-scale for energy application, such as slagging, fouling, agglomeration, and corrosion. The characteristic of high-potassium content in biomass is largely responsible for these ash-related issues. Hence, much work on coal and biomass has been performed and is still ongoing. Both biomass and Zhundong coal are high-alkali solid fuels, and it is possible that similar chemical properties and thermal behaviors exist. A comparative study is of crucial use and necessity for Zhundong coal and biomass.

The chemical properties of biomass and coal present crucial influences on reactivity [21–23], pollutant emissions (NO_x, SO_2, and PM) [24,25], fouling, and corrosion [26,27], which are of great importance for the utilization of solid fuels. It is also necessary to capture the correlations of chemical properties with parameters from direct measurement. However, the comparison of chemical properties of high-alkali biomass and coal has not been sufficiently performed yet. To date, a few studies have been carried out on correlations of chemical properties within coal or biomass. Khoshjavan et al. [28,29] probed the influences of coal chemical properties on coal swelling index and hardgrove grindability index (HGI) according to artificial neural networks with 300 datasets. The correlations between Wits-Ehac index and inherent

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Nomenclature

A_{ar}	ash content of as-received basis, %
A_d	ash content of dry basis, %
A_d^l	the lower limit of A_d, %
A_d^u	the upper limit of A_d, %
C_d	carbon content of dry basis, %
DT	deformation temperature of ash, °C
FC_d	fixed carbon content of dry basis, %
FC_d^l	the lower limit of FC_d, %
FC_d^u	the upper limit of FC_d, %
FC_{daf}	fixed carbon content of dry ash-free basis, %
FT	fluid temperature of ash, °C
Fuel ratio	ratio of fixed carbon content to volatile matter content of dry ash-free basis
H_d	hydrogen content of dry basis, %
HT	hemispherical temperature of ash, °C
M_{ad}	moisture content of air dry basis, %
M_t	total moisture content, %
N_d	nitrogen content of dry basis, %
O_d	oxygen content of dry basis, %
S_d	sulphur content of dry basis, %
ST	softening temperature of ash, °C
V_d	volatile matter content of dry basis, %
V_{daf}	volatile matter content of dry ash-free basis, %

Subscripts

ar	as-received basis
ad	air dry basis
d	dry basis
daf	dry ash-free basis
t	total

coal properties for Witbank coalfield were explored by Uludag using quite limited data [30]. Mathews et al. [5] reviewed the correlations addressing multiple coal properties with elemental compositions. They evaluated over 40 correlations for the prediction of coal parameters (such as calorific value, volatile matter, vitrinite reflectance, and aromaticity) and behaviors (including HGI, thermal swelling, direct liquefaction, etc.) against a subset of the Penn State University Coal Sample Bank and Database and indicated that challenges remained to predict the properties accurately over a wide range, but might obtain some trends. Our previous study was aimed at the correlations of coal chemical properties based on database of real-time data (data of coal samples collected from power plants or coalfields, or analyzed in our laboratory, but not from literatures) [4], but without focusing on high-alkali solid fuels or capturing the comparison between Zhundong coal and biomass. With regard to biomass, the correlations between soil and biomass chemical properties have been investigated [31–33]. Tao et al. [34,35] conducted a data synthesis of biomass properties based on literature data of energy properties (including 742 datasets from more than 144 species) and ash elements (including 367 data subjects) using principal component analysis, but the samples were restricted to biomass.

The correlations of chemical properties of solid fuels based on large database have the potential to obtain more universal results than conclusions from several datasets. However, the quantitative correlations among chemical properties of high-alkali coal and biomass from large datasets are still lacking. Less work has been conducted based on database but mainly from single or several samples with loss of certain generality. Little research was conducted to compare Zhundong coal and biomass. Our previous research mainly focused on coal, but did not specially refer to biomass or Zhundong coal. In addition, further exploration of growing region influence on the quantified correlations of chemical properties is also necessary, which was rarely investigated previously. The fuel ratio distribution of high-alkali solid fuels has yet to be fully understood. The analysis from database can supply beneficial information for a better capturing the possible quantitative correlations of chemical properties. Based on typical agricultural biomass and Zhundong coals in China, the present research will be aimed at elucidating the correlations of chemical properties within high-alkali solid fuels. The ternary distributions of the main oxide ash components were also compared. The possible quantitative correlations were further evaluated with some quantified expressions obtained. The present study can supply beneficial knowledge for describing the variation in chemical properties among and within the different varieties of high-alkali biomass and coal and the correlations between different chemical properties.

2. Materials

Zhundong high-alkali coals (denoted as ZD in figures, hereafter) and six types of typical agricultural biomass in China, including rice husk (RH), cotton straw (CS), rice straw (RS), wheat straw (WS), corn straw (COS), and corncob (COB), were selected for the present study. Biomass can be classified into four categories according to its source, mainly composed of agricultural, woody, excrement, and waste biomass. The woody, excrement, and waste biomass were outside the present scope, while the comparison between Zhundong coal and agricultural biomass was primarily focused on here. The datasets of > 100 biomass samples across China and > 10 coal samples from Zhundong coalfield were collected from both literature and real-time data (analyzed in our laboratory), while the database was composed of ~2000 data. Several national standards of China and ASTM standards were mainly applied to determine the chemical properties of solid fuel samples to ensure the data were comparable. Because the moisture content of biomass varies dramatically and is also largely influenced by storage and transportation, the moisture content is difficult to quantitatively be compared and thus all biomass properties were based on dry basis. Although the datasets of biomass and coal samples were collected over China, the results obtained have the potential to supply benefits for demonstrating the correlations among chemical properties of high-alkali solid fuels worldwide.

3. Results and discussion

3.1. Correlations between chemical element properties

Van Krevelen diagram could be applied to differentiate solid fuels with different chemical properties by correlating atomic ratio of H/C (hydrogen index) to atomic ratio of O/C (oxygen index) [5,36]. Fig. 1 shows the Van Krevelen diagram of various biomasses and Zhundong high-alkali coals, where the small black circles represent various coals in China [4]. Van Krevelen diagram clearly illustrates the comparison between hydrogen and oxygen based on carbon content. It can be seen from Fig. 1 that the correlations between H/C ratio and O/C ratio among various biomasses and coals present significant differences. Compared with coal, biomass is clearly further from the origin of the Van Krevelen diagram, which is expected and consistent with previous literatures [36–38]. The higher fraction of hydrogen and oxygen in biomass, in comparison to coal, brought about its lower heating value possibly due to the lower energy contained in C—O and C—H bonds than that in C—C bonds [38]. In addition, biomass establishes a more scattered distribution than coal in Van Krevelen diagram, especially rice straw, corn straw, and rice husk. The majority (~75%) of agricultural