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Impact of biomass addition on organic structure and mineral matter of char during coal-biomass co-gasification under CO_2 atmosphere

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ABSTRACT

To study the transformation of organic structure and mineral matter in coal-biomass mixtures during co-gasification, the anthracite and rice straw addition with different ratios were isothermally gasified at 1100 °C under CO_2 atmosphere in a fixed bed reactor. The phase-mineral composition, morphology and organic structure of solid residues produced at different gasification time were analyzed by X-ray diffraction, scanning electron microscopy coupled with energy dispersive spectrometer, Raman spectroscopy and other methods. Results revealed that the organic structure was changed in char as it became less ordered with the addition of biomass. The bulk concentrations of K and Na and their bearing minerals and phases in char increased with the addition of biomass during gasification process. The transformation of mineral matter played a significant role in promoting the coal gasification.

1. Introduction

The attention on bioenergy as an alternative to fossil energy has increased recently because of global warming problems originating mostly from fossil fuels combustion. The perspective of increasing large-scale thermo-chemical conversion of biomass and its co-processing with coal seems to be one of the main drivers for biofuel promotion at present [1]. Additionally, it is widely accepted that the solid fuel gasification will be at the heart of future generations clean technology plants for several decades. Therefore, coal-biomass co-gasification offers one of the most versatile and relatively cleaner ways to convert these solid fuels into electricity, transportation fuels, hydrogen and other energy forms. Some of the major challenges related to coal-biomass co-gasification are to achieve high carbon conversion and less ash deposition and slagging in the reactor and gas cooler equipment.

Aside from the immediate environmental and economic benefits, numerous investigations found synergies during coal-biomass co-gasification. For example, Yuan et al. [2] gasified blended chars derived from bituminous coal and rice straw at mass ratios of 4:1, 1:1, and 1:4 in CO_2 using a thermo-gravimetric reactor. It was found that the low mass ratio of biomass blending could increase the gasification rate. Jeong et al. [3] conducted co-gasification of coal-biomass char in a lab-scale tube furnace at mass ratios of 4:1, 1:1, and 1:4 in CO_2 as each blended fuel was co-gasified under the temperatures of 900, 1000 and 1100 °C. It was identified that the reactivity of char was improved with an increasing amount of biomass. Zhang et al. [4] investigated the co-gasification of different coals and biomasses using a congruent-mass thermo-gravimetric analysis. The results revealed that a synergy occurs for different mixed materials during formation of biomass ash. Similar findings were reported by Krerkkaiwan et al. [5] and Masnadi et al. [6]. In contrast, an inhibitory action during co-processing of coal and biomass was also reported. For instance, Ding et al. [7] suggested that the inhibiting effect was due to the intimate contact and comparable gasification rate between biomass and coal. Habibi et al. [8] explored switchgrass-coal mixtures and showed a deactivation effect due to the formation of aluminosilicates. Similar views were reached by Masnadi et al. [9]. They drew the conclusion that the synergy or inhibition was associated mostly with alkali metal and silicon components occurring in these solid fuels.

The importance of the variable inorganic constituents and their behavior during thermo-chemical conversion of coal [10,11] and biomass [1,12,13] have been studied and summarized. Skodras

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et al. [14] found that the inorganic constituents in coal play a controlling role in determining the gasification reactivity because a reasonably good correlation exists between the alkali index and the gasification index. Other studies [15–17] showed a significant variation of gasification rate attributed to the mineral matter present in coal. Ellis et al. [18] gasified mixed chars from biomass and coal at 800 °C. They observed a lower co-gasification rate because the inorganic matter in this mixture interacted to form Ca aluminosilicate (gehlenite) which inhibited the gasification. The morphological change and fusion of minerals in char at high temperature also have a notable effect on gasification reactivity because the catalytic action of minerals associates with their contact area with carbon particles [19,20].

However, when the coal co-gasifies with biomass, it is not clear how the mineral matter in biomass reacts with that in coal, and how they affect the co-gasification process. The aim of the present study is to evaluate the impact of biomass addition on mineral matter and solid residue organic structure transformations during anthracite and rice straw co-gasification under CO_2 atmosphere. The mixed solid residues produced at variable coal and biomass ratios and different gasification time were investigated for that purpose.

2. Experimental

The Jincheng anthracite provided by Jincheng anthracite mining group, in Shanxi province, China, is a typical coal with high ash yield and high ash fusion temperatures. Rice straw directly collected in the field of a suburb of Taiyuan city, Shanxi province, China, were used as gasification feedstock. The samples were ground and sieved to 0.106–0.125 mm prior to the experiments. The properties of the pulverized samples are presented in Table 1. The proximate analysis followed the Chinese standard methodology GB/T 212-2008 and ultimate analysis data was obtained from a Vario EL elemental analyzer. The chemical components of ash was analyzed following the Chinese standard methodology GB/T 1574-2007, and ash fusion temperature analysis was determined using a HR-5A ash fusion analyzer (Hebi, China) under weak reduction atmosphere, according to Chinese standard GB/T 219-2008.

Table 1
Properties of samples, %.

Characteristic	Anthracite	Rice straw
Proximate analysis		
Moisture (air dried basis)	0.95	5.83
Ash (dry basis)	21.40	15.79
Volatile matter (dry ash-free basis)	10.21	85.35
Fixed carbon (dry ash-free basis)	89.79	14.65
Ultimate analysis (dry ash-free basis)		
Carbon	87.94	45.91
Hydrogen	3.22	2.88
Oxygen (by difference)	5.32	48.50
Nitrogen	1.10	0.93
Sulphur	2.42	1.78
Ash analysis		
SiO_2	49.37	42.68
Al_2O_3	31.94	5.03
Fe_2O_3	11.10	2.74
CaO	2.91	13.37
MgO	1.12	6.76
TiO_2	1.46	1.56
Na_2O	0.57	5.52
K_2O	0.80	11.45
SO_3	0.73	10.89
Ash-fusion test (°C)		
Initial deformation temperature (DT)	>1500	1090
Spherical temperature (ST)	>1500	1127
Hemispherical temperature (HT)	>1500	1130
Fluid temperature (FT)	>1500	1133

The gasification and co-gasification tests were performed in a tubular quartz tube reactor with size of 26 mm for the outer diameter and of 1000 mm length. The corundum boat (with length of 88 mm, width of 15 mm and height of 9 mm) with the samples were pushed into the center of the quartz tube when the furnace was heated to 1100 °C. The samples used include the anthracite (80 mg) and different proportions of rice straw (20, 40, 60 and 80 mg), and they were gasified under CO_2 atmosphere with a flow rate of 200 mL/min. Hence, the biomass addition ratio is 20%, 33%, 43% and 50%, respectively. The gasification residues obtained at different gasification time, namely 1, 3, 5, 7, 10, 15, 20, 30 and 40 min, were pulled out from the reactor, and then quenched on the top of an ice cooled iron in a desiccator to prevent phase transformation and crystal segregation of mineral matter [19]. The oxidation of Jincheng char was limited under static air due to the low reactivity and low volatility of anthracite. The data for particle size, sample mass and CO_2 flow rate from preliminary gasification experiments were used to exclude the internal and external diffusion. The weight loss was calculated based on the fuel and residue masses using the Eq. (1), where: the symbol $M_{\text{mixed residue}}$ denoted as mass (in mg) of mixed char produced at different gasification time; $M_{\text{biomass residue}}$ denoted as mass (in mg) of biomass char during biomass gasification alone at different gasification time; and M_{coal} denoted as mass of raw coal (80 mg).

$$Weight\ loss\ \% = 1 - \frac{M_{mixed\ \ residue} - M_{biomass\ \ residue}}{M_{coal}} * 100\% \qquad (1)$$

A confocal Raman microscope spectrometer was used to analyze the organic structures of the char samples. The excitation source was an Ar-ion laser with 20 mW output power and 514.5 nm excitation line. The laser power was set at 10 mW on the surface of samples. Extended scans from 800 to 2000 cm^{-1} were used for the first-order Raman spectrum. The tested char samples were analyzed at least three points across the sample surface. A Rigaku's Ultima IV type X-ray diffractometer (XRD) was used to study the mineral matter of char samples with the following diffraction conditions: Cu Kα radiation, tube current of 40 mA, tube voltage of 40 kV and a scan rate of 4°/min between 10° and 90° 2θ. A HITACHI-TM 3000 scanning electron microscope (SEM) equipped with a Brook's QX 70 energy dispersive X-ray analyzer (EDX) at an accelerating voltage of 15 kV was used to study the char samples morphology and element composition on the sample surface. To improve the quality of the analyses all the samples were covered by sputtering a thin Au-Pd coat to ensure surface conductivity.

3. Results and discussion

3.1. Chemical composition of coal and biomass

The data from proximate, ultimate and ash analyses, as well as from ash-fusion test of the anthracite and rice straw show that these solid fuels have different properties (Table 1). It can be seen that the rice straw and its ash has higher values of moisture, volatile matter, O, CaO, MgO, TiO_2, Na_2O, K_2O and SO_3, and lower values of ash yield, fixed carbon, C, H, N, S, SiO_2, Al_2O_3, Fe_2O_3, and ash-fusion temperatures in comparison with the anthracite and its ash. Such differences are typical for coal and biomass and they provoke the diverse behavior of both fuels during their thermochemical conversion [1,13].