



Influence of volatiles-char interactions between coal and biomass on the volatiles released, resulting char structure and reactivity during co-pyrolysis



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ABSTRACT

The volatiles-char interactions are an important phenomenon in almost all existing pyrolysis/gasification processes. These interactions can affect almost all aspects of pyrolysis/gasification processes significantly. This study explores the influence of the volatiles-char interactions between the coal and biomass on the volatiles released, the resulting char structure, and the reactivity during co-pyrolysis. The interactions of biomass pyrolysis volatiles-nascent coal char and coal pyrolysis volatiles-nascent biomass char were studied at 800 °C in a two-stage fixed bed reactor. The product yields, gas composition, tar composition, Raman structure, and gasification reactivity of the resulting char were investigated. The results show that the presence of char promoted tar conversion into non-condensable gases during the volatiles-char interactions between the coal and biomass. For biomass volatiles with coal char interaction, the gas products were CO₂, CH₄, and CO whose concentrations decreased, and H₂, whose concentration increased. Concerning the liquid products, the ketones, esters, phenols, and furans contents increased, whereas the aromatics content decreased. However, for coal volatiles with biomass char interaction, the concentrations of CO₂ and H₂ in the gas products and the content of furans in the liquid products showed the opposite trend. In addition, in the presence of biomass or coal volatiles, the larger aromatic ring systems in coal or biomass char grew, resulting in a decrease in the gasification reactivity. The volatiles-char interactions had a stronger influence on decreasing the reactivity of coal char than biomass char.

1. Introduction

In the past few decades, the utilization of coal has led to an alarming rise in emissions of CO₂, NO_x, and SO_x [1,2]. Biomass is considered an environmentally friendly fuel because it is a renewable energy source and contains less sulfur than coal [3–5]. However, biomass also has some disadvantages, such as lower energy density and wide distribution [6,7]. Some of these problems can be overcome by the co-gasification of biomass and coal [8–10]. Co-pyrolysis is the initial step in the co-gasification process, but the process influences the subsequent reactions significantly and affects the whole co-gasification performance [11–13]. A full understanding of the co-pyrolysis process would help the development of highly efficient co-gasification technology.

Most current research focuses on the co-pyrolysis characteristics of coal with biomass. Haykiri-Acma and Yaman [14] found that the addition of thermally reactive hazelnut shells led to some increases in the volatilization rates of coals, especially at temperatures below 500 °C.

Yuan et al. [15] reported that the rapid co-pyrolysis of rice straw and a bituminous coal resulted in decreased char yields and increased volatile yields. Wei et al. [16] stated that the inhibition effect of co-pyrolysis on the co-gasification reactivity of the char weakened with increasing biomass proportion and gasification temperature. In their work, a synergy between the coal and biomass was often observed, which was beneficial for the overall co-thermochemical performance. Thus, further research on such synergy is very important to understand the co-thermochemical process better. Kerkkaiwan et al. [17] and Song et al. [18] proposed that the synergetic effect could be attributed to the alkali and alkaline earth metallic species (AAEMs) in the biomass. In addition, the volatiles-char interactions are important phenomena in almost all existing pyrolysis/gasification processes, and can significantly affect the tar destruction and the structure and reactivity of the resulting char [19]. Because of the significance of the co-pyrolysis process on the whole co-gasification performance, further investigation on how the volatiles-char interactions influence the co-pyrolysis, as well as the role

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of AAEMs, is needed. Matsuhara et al. [20] and Song et al. [21] reported that tar is converted into non-condensable gases and coke by char during coal or biomass pyrolysis. However, there has been little research on the volatiles-char interactions between coal and biomass during co-pyrolysis. Thus, the effects of char on in situ pyrolyzed volatile vapors during coal/biomass co-pyrolysis also requires further research.

Char can be considered a catalyst as well as an adsorbent for tar removal [22]. Liu et al. [23] and Paethanom and Yoshikawa [24] showed that bio-char exhibits a higher adsorption capacity for phenol and tar molecules. Zhang et al. [25] and Song et al. [21] found that biomass char catalytically destroys the tar molecules from biomass pyrolysis or gasification during the volatiles-char interactions. The conversion of tar using char as a catalyst can be performed by in situ catalysis in the gasifier or ex situ catalysis in the reformer in the real gasification system. These previous studies mainly focused on the catalytic role of char on tar removal in biomass pyrolysis or gasification; however, the effect of different chars on the volatiles, including tar and non-condensable gases during the co-pyrolysis of coal and biomass has not been clarified, which is important for the development of environmentally friendly and highly efficient gasification technology.

Notably, the volatiles have an important effect on char structure evolution, and many researchers have investigated char structural evolution during coal or biomass pyrolysis/gasification [26]. Li et al. [27] studied the gasification of Collie sub-bituminous coal and showed that the char structure changes drastically with different gasification agents. Besides the non-condensable gases, the volatiles including tar, are also believed to influence the char structure. Zhang et al. [28] found that the coal char structure changes because of volatiles-char interactions during the steam gasification of Victorian brown coal. However, the structural evolution of char derived from the volatiles-char interactions between coal and biomass during co-pyrolysis has not been reported. Because the reactivity of char is related to its structure, the resulting char structure should be examined to obtain a better understanding of the co-pyrolysis/gasification of coal and biomass.

The study of co-pyrolysis as the first step of the coal and biomass co-gasification process is crucial [29]. Thus, the objective of this study was to explore the influence of the volatiles-char interactions between coal and biomass on the volatiles released, the resulting char structure and reactivity during co-pyrolysis in a two-stage fixed bed reactor. The product yields, gas composition, and tar composition during the volatiles-char interactions at different sample mass ratios were investigated, and the Raman structure and gasification reactivity of the resulting char were analyzed. The results of this study may give a better understanding of the volatiles-char interactions between coal and biomass during co-pyrolysis and will provide significant fundamental support and theoretical guidance for process design and optimization and the control of the products distribution for the co-conversion industrial applications.

2. Materials and methods

2.1. Experimental materials

Rice straw and Shenmu bituminous coal from China were selected as biomass and coal samples, respectively. The samples were pulverized to less than 0.125 mm and dried at 105 °C for 24 h before each trial. The proximate and ultimate analyses were performed using a TGA2000 thermogravimetric analyzer (Las Navas, Spain) and a C/H/N/S analyzer (EL-2, Vario, Germany), respectively. The low heating value (LHV) was analyzed using a bomb calorimeter (Parr 6300, USA). The results of these analyses are shown in Table 1. The rice straw showed higher volatile and ash contents but a lower fixed carbon content than coal. The ash composition was determined using an X-ray fluorescence spectrum analyzer (XRF, Eagle III, EDAX Inc.) and the determined oxide contents are shown in Table 2. The main inorganic components of rice

straw were Si and K, whereas those of coal were Ca, Si, Al, S, and Fe.

2.2. Experimental setup and methods

The interactions of volatiles and chars were performed in a two-stage vertical reactor system, as shown in Fig. 1. The reactor consisted of a quartz tube with an internal diameter of 40 mm and a total height of 765 mm. Coal or biomass pyrolysis was carried out in reaction zone 1, then, the pyrolytic vapor passed to reaction zone 2 and interacted with the nascent char particles. The experiment can be divided into two parts. First, coal or biomass pyrolysis resulted in the formation of nascent char. Both reaction zones of the electrical furnace were pre-heated and stabilized at 800 °C. A quartz basket (with an outside diameter of 38 mm and a multi-orifice plate bottom) containing coal or biomass samples was placed on an inner annular plate (as a support for the basket) of the reactor in reaction zone 2 to ensure that the volatiles from reaction zone 1 had to pass through and react with the char bed in reaction zone 2. N₂ (purity > 99.999 vol%, 200 mL min⁻¹) was supplied as a carrier gas to maintain an inert environment. Then, the reactor was quickly moved into an electric furnace and heated for 10 min to obtain the nascent char. Second, the biomass or coal pyrolytic vapors interacted with the nascent coal or biomass char. Once the nascent char had been obtained, the condensers were connected to the tail of the reactor. Meanwhile, another hanging basket (loaded with dried biomass or coal) was immediately placed in reaction zone 1 of the reactor and devolatilized for 15 min. Then, the pyrolytic vapors passed to reaction zone 2 and interacted with the coal or biomass char.

During this interaction process, the gaseous products were condensed using condensers maintained at 0 °C in an ice bath to collect the condensable tar, and the non-condensable gases were collected with a gas bag after drying. The gas yield was defined as the mass ratio of the gaseous products to the raw sample. After each experiment, the reactor was removed from the furnace for air-cooling, with a continuous flow of N₂ to ensure the cooling of the solid sample in an inert atmosphere. The solid residual char in both baskets was collected at room temperature and was weighed to determine the final char yield (based on the raw sample mass). The tar yield was determined with the weight difference of the condensers before and after the experiment.

In this study, the “mass ratio” refers to the ratio of the amount of nascent char producer (raw fuel) to the total amount of the pyrolyzing material and the nascent char producer (raw fuel). Here, this ratio varied from 0% to 100%. During each trial, the mass of the nascent char producer was fixed at 2 g, except when the mass ratio was 0%, in which case, the mass of the volatiles provider was 2 g. Each experiment was conducted at least twice to obtain the average values, and the standard deviation for various product yield was within 5%.

The proximate and ultimate analyses and pore structure characteristics of the nascent rice straw char and coal char before interactions with the volatiles are shown in Tables 3 and 4, respectively. As shown in the tables, the volatiles content in the char was very small relative to that in the raw sample for both rice straw and coal, and the average pore size of the rice straw char was larger than that of coal char.

2.3. Product characterization

2.3.1. Gaseous products

The gaseous products were determined using a gas chromatograph (Agilent, Micro-GC 3000A, USA) equipped with a thermal conductivity detector (TCD). Channel A contained molecular sieve 5A for detecting H₂, CO, and CH₄ at 110 °C, and channel B was a PLOT U column for the detection of CO₂ at 105 °C. The gas yield was calculated using the N₂ balance.

2.3.2. Liquid products

Chemical compounds in the condensable tar in the condensers dissolved in acetone were identified using a gas chromatograph coupled

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