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Research Paper

Effects of coal pretreatment on the products of co-pyrolysis of caking bituminous coal and corn stalks mixed in equal proportion

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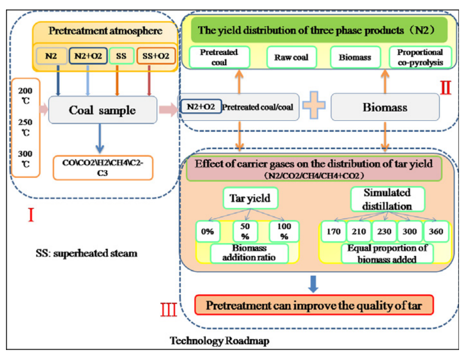
HIGHLIGHTS

- The effect of destroying the caking property of coal samples was the best in the aerobic atmosphere.
- The influence of the pretreatment of the mixed gas on the co-pyrolysis product evolution was investigated.
- The yield of tar produced by proportional co-pyrolysis of pretreated coal sample and corn stalk was increased.
- The mixed carrier gas of $CH_4 + CO_2$ was conducive to improve the quality of tar.

GRAPHICAL ABSTRACT



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ABSTRACT

Aim at the problems that the higher heavy tar yield of caking bituminous coal (CBC) pyrolysis and the synergistic effect of its co-pyrolysis with biomass. The changes of gas evolution during the pretreatment process of CBC with oxygen in the atmosphere, and the strengthening effects of the co-pyrolysis of pretreated coal sample and corn stalk mixed in equal proportion on the pyrolysis products under different carrier gases were studied in this paper. With the increase of the pretreatment temperature, more gas products were obtained than superheated steam from the pretreatment in nitrogen, while yield of gases such as CO_2 and CO were much higher with oxygen in the atmosphere and the yield of CO_2 increased most. The effects of pretreatment on the destruction of the caking property enhanced as the pretreatment temperature increased with oxygen in the atmosphere, which was beneficial to coal sample pyrolysis reaction, resulting in a 7.01% lower pyrolysis char yield than raw coal char. The equal proportion co-pyrolysis had a synergistic promoting effect on the formation of H_2, CO_2 and CH_4. Compared with other carrier gases, light tar content increased significantly in the mixed carrier gas of $CH_4 + CO_2$, while the improvement in tar quality should be attributed to the fact that content of phenol oil and anthracene oil increased and the content of asphaltene decreased obviously.

1. Introduction

Coal and biomass are both important in China's energy resource structure. Coal is one of the dominant energy in China, with abundant reserves. Biomass is also one of the most abundant and promising renewable energy sources and is considered as CO_2 neutral with low contents of sulfur [1]. In practice, however, the yield of fine chemicals and fuel obtained from coal is quite limited because of the lower hydrogen-carbon ratio. As a hydrogen-rich renewable resource, biomass can be used as a cheap source of

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hydrogen for coal pyrolysis to improve the yield of volatile matter, which has far-reaching significance in alleviating energy shortage and adjusting the energy structure [2–4]. The deep analysis and comparison study on the synergetic effects of the co-pyrolysis of coal and biomass has been intensively carried out. It is worthwhile mentioning that a number of researchers have stated that the catalytic effects of the minerals in biomass could promote the synergy effects between biomass and coal [5–7]. However, some other researchers have obtained quite contrary results [8,9]. The existence of synergy effects may depend on the experimental conditions (temperature, pressure, heating rate and contact intensity), types of the samples and the experimental device, etc. [10,11]. Although there is controversy about synergistic effect in the co-pyrolysis process, a common understanding is that the co-pyrolysis of coal and biomass can improve tar quality. Therefore, the co-pyrolysis of coal and biomass has been the focus of the energy and chemical industry, in order to produce high-quality fuel, by adopting small experimental equipment such as thermal gravimetric analyzer, fixed bed and fluidized bed.

During the co-pyrolysis of coal and biomass, gas, liquid and solid products are influenced by the feedstock properties and operating conditions together [12]. For example, in addition to the synergistic effect found in the co-pyrolysis process of lignite and rice bran, Yang et al. [10] have also found that the addition of rice bran can obviously affect the yield of three phase products, and promote the gasification of char as well as the reaction between the gas products which is caused by the secondary decomposition of tar. Notwithstanding the various catalytic mechanisms that have been proposed to explain the synergy effect, they mainly focus on the catalysis of alkali or alkaline earth metals (AAEM) in coal and biomass and the hydrogen transfer during co-pyrolysis process. Specific mechanisms of co-pyrolysis of different kinds of biomass and coal, including the role of catalytic AAEM and the hydrogen donor source, have not yet been clarified. Wu et al. [11] discovered that cellulose and carboxymethylcellulose sodium (CMC) exhibited different impacts on the co-pyrolysis behavior. Positive char yield synergistic effects were observed during the co-pyrolysis of cellulose and bituminous coal, with less char generated at temperature above 360 °C.

However, it is difficult to apply the co-pyrolysis of caking bituminous coal and biomass, as the existing technology is applicable to lignite, long flame coal and some low-grade bituminous coal. Therefore, to investigate the effects of caking bituminous coal pretreated with oxygen in the atmospheres on the co-pyrolysis and to characterize the product properties, there is still a lot to study on the co-pyrolysis of coal and biomass.

In China, the pulverized caking bituminous coal is partly used for direct combustion to generate heat, electric power and so on, in a not very efficient or effective way. And the rest of the pulverized caking bituminous coal is generally stacked on the ground within the plant, which is a waste of resources and could cause environmental pollution. Low temperature pre-oxidation can be used to destroy the caking propensity of caking bituminous coal. It is a potential approach to utilize the spare pulverized caking propensity and the biomass as a feedstock for co-pyrolysis. Such studies have been conducted with focus on the particles of caking bituminous coal in gasification via representative gasifiers, including high-temperature Winkler gasifier, Enda gasifier, ash-agglomeration fluidized bed gasifier, U-gas gasifier and so on. The particles of caking bituminous coal may bond together in the dense phase bed or on the furnace wall, leading to serious coking reactions because the coal particles could not be properly fluidized [13–16]. As the basic and necessary stage of thermal conversion of coal, pyrolysis has an important impact on gasification, liquefaction, combustion and other processes [17–19]. Therefore, it is important for the caking property of caking bituminous coal to be destructed through pretreatment to reduce the caking index of coal particles in the pyrolysis process, and further to improve the combustion and gasification rate. Considerable research have made efforts to reveal how the pretreatment can destroy the caking propensity of caking bituminous coal. Zhang et al. [20] have found that coal with the caking index of about 20 could be successfully gasified in jetting pre-oxidation fluidized bed gasification plant using normal air, O_2-enriched air, and the caking index decreased by rising the oxygen percentage applied to the jet feeding. Furthermore, Zhao et al. [21] found that without oxygen in the jetting gas, it would be impossible to fully destroy the caking property of the coal, even at sufficiently high temperature. Forney et al. [22] pretreated a strongly fine coals and destroyed the caking properties of the coal with a kind of fluidizing gas which was either steam containing at least 0.2 vol% oxygen or inert gas, at temperature of 673–698 K in a bench-scale fluidized bed reactor. This results indicate that the caking propensity of fine coals characterized by the free swelling index, decreased to values below 2, and the minimum time required to produce a completely non-agglomerating char was about 5 min.

Related studies have investigated the co-pyrolysis of lignite, bituminous coal and biomass, the destruction of the caking property of caking bituminous coal by pre-oxidation at low temperature, and the effects of different carrier gas composition on the distribution and property of the pyrolysis products. These studies mainly focus on the experimental comparison of the effects of coal category, the proportion of the biomass added, final pyrolysis temperature and other factors on the yield of products. In addition, the co-pyrolysis kinetics, property of tar and the gasification reaction characteristics of char produced from the co-pyrolysis of biomass and coal, has also been studied. Many valuable experimental results have been obtained [3,12,23–25]. However, few research has reported on the effects of the destruciton of caking property through pretreatment in the co-pyrolysis of caking bituminous coal and biomass on the property of the pyrolysis products.

The aim of this paper is to investigate the gas evolution and tar characteristics of the caking bituminous coal under different atmospheres at difference temperature, and the effects of the pretreatment by superheated steam or N_2 with and without O_2, after which the caking property was destructed, on the gas yield and the product distribution of co-pyrolysis of coal and biomass in different carrier gases, and quality of tar-gas mixture. The experiments were conducted using a lab-scale fixed-bed, a thermogravimetric analyzer (TGA) and a simulated distillation analyzer (Agilent7890A).

2. Experimental materials and methods

2.1. Experimental samples

In this experiment, the coal sample was collected from the No. 3 coal seam of Zichang County, Shanxi province (Hereafter called CBC). The corn stalks were collected in the countryside of Miyun, Beijing. In the first place, the samples were crushed to below 1 mm by high-speed crusher and sieved by 80 mesh standard screening. Then, the samples were placed and labeled in sealed containers and stored in a refrigerator after having been dried for 2 h at 105 °C under vacuum condition. At last, the particle size of the raw coal was less than 80 mesh. The proximate and ultimate analyses were conducted according to Chinese National Standards GBT212-2008, results given in Table 1. The raw coal and biomass were incinerated according to Chinese National Standard GB-T/483. The yield of the products was calculated on dry ash free