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Pyrolysis behavior of corncob and coal gangue with modified medical stone and HZSM-5 based additives

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ABSTRACT

Pyrolysis behavior of coal gangue and corncob with some additives was studied in a fixed bed reactor. The results showed that with the blending ratio of coal gangue increasing during pyrolysis, the liquid oil yield and the gas yield all decreased, and there were interactions between coal gangue and corncob during co-pyrolysis. Furthermore, the results also showed that just as HZSM-5, medical stone (MS) also had an important influence on the pyrolysis process and could increase the liquid oil yield. Adding Co/MS, Mo/MS, PW_{12}/MS, KCl/MS, $CaCl_2$/MS and Co-Mo/MS could increase the oil yield, and Co/MS had a better effect on liquid oil properties than other additives. Adding $CaCl_2$/MS and Mo/MS also could increase the relative content of H_2 during co-pyrolysis. Adding HZSM-5, KCl/HZSM-5, $CaCl_2$/HZSM-5, $SnCl_2$/HZSM-5, Co/HZSM-5, PW_{12}/HZSM-5 and Mo/HZSM-5 also made the liquid oil yield increase and the gas yield decrease during co-pyrolysis at 500 °C and 900 °C; and Co/MS also had a better effect on liquid oil properties than other additives.

1. Introduction

As have been known, coal gangue is the main industrial solid waste (approximately 10–15% of the total coal production) produced during coal mining [1]. Up to now, about 3 billion tons of coal gangue has been produced over the years in China. Mountains of coal gangue not only occupy land and affect the ecological environment, but also pollute the surrounding soil and groundwater [2]. At the same time, the harmful gas produced from coal gangue spontaneous combustion also causes air pollution. Therefore, how to use coal gangue efficiently has been paid more and more attentions.

There are many studies about coal gangue thermal treatment. Zhang et al. showed that the ignition temperature, characteristic DTG curves and activation energies of coal gangue were affected by feedstock properties [3]. Meng et al. found that increasing of the O_2 partial pressure and combustion temperature led to an increase of the coal gangue burnout rate [4]. Ren et al. found that the mass loss decreased and comprehensive combustion characteristic index increased slightly when CH_4 is present in the combustion atmosphere with equivalent O_2 concentration [5]. Zhou et al. concluded that the transformation behavior of mineral phase of coal gangue mainly relied on the combustion temperature, and the volatile matter ratios of selected trace elements increased with combustion temperature increasing [6]. Yang et al. showed that during co-combustion of sewage sludge and coal gangue, a synergic effect on both desulfurization and denitrification can be expected at 800 °C [7]. Moreover, the characteristic temperature and performance parameters of coal gangue pyrolysis were obtained [8–10]. Furthermore, as have been known, biomass is a kind of resource which has the character of zero emission of carbon dioxide and can reduce greenhouse gas, and it is also a kind of renewable and clean energy resource, and can be used to replace part of the fossil fuel [11]. So studies about coprocessing of coal and biomass for reducing CO_2 emission have been paid more and more attentions [11,12]. Some literatures showed that there are synergistic interactions between coal and biomass, and synergistic effects might be due to “gas-coal” or “char-coal” interactions [13,14]. Moreover, as we have known, pyrolysis of coal and biomass could get oil, while oils obtained from pyrolysis usually present some shortcomings, such as high moisture content, high viscosity and acidity, and they are difficult to use directly. Then how to improve the quality of the bio-oil has attracted massive attentions. Some literatures demonstrated that HZSM-5 and synthesized metal/HZSM-5 enhanced the aromatic content and decreased the undesirable oxygenated and N-containing compounds [11,15]. Other reports mentioned that γ-Al_2O_3, metal/γ-Al_2O_3 and metal oxides also have the catalytic effect [16–18]. Medical stone (MS), which is a kind of natural mineral, can be used as carriers of catalysts due to its special properties, such as the porous and spongy structure, abundant inorganic aluminosilicate content. In our previous work, the results showed that the

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presence of medical stone based additives could increase the yield of aliphatic content of liquid oil during cotton seed liquefaction [19]. Then we infer that medical stone based catalysts and metal/HZSM-5 maybe also has effects on the product distributions during pyrolysis of coal gangue and biomass. As a kind of biomass, corncob is abundant due to that corn is widely planted in China; and on the other hand, the photosynthesis of corn is very strong that it can consume a great deal of carbon dioxide. So in our paper, corncob was used as the biomass source.

In this work, the pyrolysis behavior of coal gangue and corncob was investigated in a fixed-bed reactor. The novelty of this paper is: using medical stone based catalysts and metal/HZSM-5 as additives, and study on the effect of them on the product distributions and characters of the oil during co-pyrolysis of corncob and coal gangue.

2. Experimental

2.1. Materials preparation

The coal gangue was from Lu'an coal mine in Shanxi Province of China, and the corncob used was collected from Linfen in Shanxi Province of China. Because the samples were large particles (much larger than 0.25 mm), so the samples were pulverized firstly, and then sieved by 0.25 mm and 0.15 mm sieves; and finally, the pulverized samples were dried at 105 °C for 24 h [19,20]. Due to that the particles in 0.15–0.25 mm were dominant, so the samples with size of 0.15–0.25 mm were used in the experiment. The proximate and ultimate analyses of the samples with size of 0.15–0.25 mm were presented in Table 1, and the ash elemental analysis of the coal gangue was presented in Table S1. The medical stone (MS) used was purchased from Linshou in Hebei Province of China, and HZSM-5 was from Langfang in Hebei Province of China. The compositions of the medical stone is the same as that reported in our previous work [20], and the Si/Al ratio of HZSM-5 is 30. The composited additives were prepared by the methods of conventional incipient wetness impregnation [18]. Firstly, $CaCl_2$, $SnCl_2{\cdot}2H_2O$, KCl, $Co(NO_3)_2{\cdot}6H_2O$, $(NH_4)\ Mo_7O_{24}{\cdot}4H_2O$, $Ni\ (NO_3)_2{\cdot}3H_2O$ and $H_3PO_{40}W_{12}$ (PW_{12}) (purchased from Tianjin Guangfu Technology Development CO., LTD, China) were dissolved in distilled water respectively, and then carriers were added. Finally, the mixtures were dried at 105 °C for 4 h, and then calcined at 500 °C for 6 h. The characterizations of additives were analyzed by X-ray powder diffraction (Rigaku Ultima IV) with Cu Ka radiation.

2.2. Experimental equipment and procedure

The pyrolysis experiments were carried out in a fixed-bed reactor. During the experiments, the nitrogen gas was used as carrier gas with the flow rate of 200 ml/min. Each time, 10.00 g of sample or 10.00 g of sample with 1.00 g of additive was put into the reactor, and the sample was mixed with the additive uniformly. The reactor was heated to the desired temperature at a rate of 10 °C/min and then hold for 30 min. After reaction the reactor was cooled to room temperature and then the products were taken out for further analysis. During the experiment, the liquid products were collected by two groups of liquid containers (three conical flasks in each group), which were all put into the cold trap; and the gas obtained from pyrolysis will go through the liquid containers, and then the condensable gases were condensed and collected; further, the water in the oil was removed by centrifugalization. The experiments were performed three times, and the experimental values were the average of the three times; and the experimental error is less than 1.0%.

Table 1
Proximate and ultimate analysis of samples (ad, wt%).

Samples	M_{ad}	A_{ad}	FC_{ad}	V_{ad}	C	H	O[a]	N	S
Corncob	4.97	2.06	12.38	80.59	44.3	6.08	41.91	0.62	0.06
Coal gangue	0.95	82.13	6.92	10	12.82	1.38	2.12	0.40	0.20

[a] By difference.

2.3. Analysis of the products

The liquid oils were analyzed by Nuclear magnetic resonance (^1H NMR, ^{13}C NMR; Ascend™600, Bruker, Germany), Fourier transform infrared spectrometer (FTIR, Varian 640, Varian Associates, USA) and gas chromatography–mass spectrometry (GC/MS, Polaris Q, Thermo Fisher, USA), and the gases were analyzed by gas chromatograph (Agilent 7890A, Agilent Technologies, USA).

2.4. Calculation methods

The yields of the liquid oils and the residuals (include the additive) were calculated by the Eqs. (1) and (2), and the gas yield was calculated by difference.

$$Liquid\ oil\ yield\ (oil\ \%) = \omega_1/\omega_0 \times 100\% \quad (1)$$

$$Residual\ yield\ (residual\ \%) = [(\omega_3 - \omega_2)/\omega_0] \times 100\% \quad (2)$$

where ω_0(g), ω_1(g), ω_2(g) and ω_3(g) were defined as the weight of the sample, the liquid oil, the additives and the residuals respectively, and the dry basis was used during calculation.

While:

$$Gas\ yield\ (Gas\ \%) = 100\% - \text{Liquid oil yield} - \text{Residual yield} \quad (3)$$

Here: Gas yield (Gas %) includes the yield of water vapor.

3. Results and discussion

3.1. Product distributions obtained from pyrolysis of coal gangue and corncob

The product distributions obtained from pyrolysis of coal gangue and corncob at different temperatures were shown in Table 2. From Table 2 one could see that for coal gangue pyrolysis, there was almost no oil when the temperature was lower than 500 °C, and at 500 °C the oil yield was 5.2%; while corncob began to crack at 200 °C, and the liquid oil yield of corncob was higher than that of the coal gangue at the same temperature. The liquid oil yield of coal gangue increased with temperature increasing and the maximum value of the oil yield was 8.30% at 900 °C; the solid residual yield decreased with temperature increasing; while the gas yield got the maximum value at 800 °C. During pyrolysis, liquid oil was produced due to the devolatilization of organic matter. Higher temperature with more energy could prompt the cracking of strong organic bonds, so the liquid oil yield increased at higher temperature. For corncob, the liquid oil yield increased firstly and then decreased, and the maximum value of oil yield was 49.9% at 500 °C; and the gas yield increased with temperature increasing; while the solid residual yield decreased continuously when the temperature increased. The results showed that at higher temperature, more gases could be produced due to secondary reactions such as thermal cracking of the volatile compounds and so on [21].

The compositions of gas were shown in Table 3. From Table 3 one could see that CO_2 and H_2 began to release at 400 °C during coal gangue pyrolysis, while they began to release at 300 °C for corncob. Whether for coal gangue or corncob during pyrolysis, at lower temperature (300 °C–400 °C), the main composition of gas was CO_2, while H_2 was the dominant composition of the gas at higher temperature (600 °C–900 °C). For corncob, CO and CH_4 were produced at 300 °C, and the content of CO decreased firstly and then increased when the temperature was higher than 600 °C, while the tendency of CH_4 was just opposite. For coal gangue, CO began to release at 700 °C, and reached the maximum value at 900 °C, which was the same as that of corncob;